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Quantum Modelling of Piezophotonic-Induced Stark Effect at Luteolin–Polydopamine–BaTiO₃ Hybrid Interfaces for Bias-Free Functional Imaging and Sensing

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ABSTRACT

Context

The pursuit of continuous, non-invasive physiological monitoring is fundamentally limited by the "wiring bottleneck" and the need for external electrical bias in conventional sensors, which introduce noise, safety risks, and signal perturbation. A transformative solution requires a transduction mechanism that is intrinsically bias-free, converting biological mechanical energy directly into a high-fidelity optical readout without electrodes or external power.

Method

Here, we introduce the piezophotonic-induced Stark effect (PISE) as a fully passive, mechanically driven optical transduction mechanism enabled by a hybrid organic–inorganic interface. The system combines the piezoelectric field generation of barium titanate (BaTiO₃) nanoparticles with the field-sensitive excited-state intramolecular proton transfer (ESIPT) photophysics of surface-anchored luteolin, linked via an ultrathin polydopamine spacer. Through a self-consistent theoretical framework spanning piezoelectric tensor analysis, Maxwell electrostatics, and quantum-confined Stark physics, we demonstrate that low-amplitude mechanical stresses (0.1–100 kPa) generate interfacial electric fields up to $\sim 10^5$ V m⁻¹, which in turn produce spectrally resolvable Stark shifts (~ 0.1 meV) and strong fluorescence intensity modulation. The mechanism operates without external bias, electrodes, or wiring, and exhibits a dynamic bandwidth exceeding 150 Hz, suitable for physiological and ultrasonic sensing. This work thus presents a general theoretical foundation for mechano-optical sensing via interfacial field effects, establishing PISE as a scalable principle for autonomous functional imaging and wearable diagnostics.

Keywords: Piezophotonic-Induced Stark Effect, Bias-Free Sensing, Quantum-Confined Stark Effect, Mechano-Optical Transduction, Interfacial Stark Effect

1.0. INTRODUCTION

The demand for continuous, real-time physiological monitoring has intensified as attention shifts toward dynamic, high-sensitivity biological environments such as fetal development, neural activity, and cardiovascular function [1-5]. Current clinical imaging modalities, including magnetic resonance imaging (MRI) and computed tomography (CT), provide exceptional spatial resolution but remain constrained by

their reliance on large, stationary instrumentation and substantial power requirements, restricting their use to episodic, clinic-based assessments rather than continuous monitoring [6-8]. As a result, extended temporal gaps persist during which transient yet clinically significant events such as fetal distress signals or rapid intracranial pressure fluctuations may go undetected, motivating sustained interest in improved physiological surveillance strategies during pregnancy and other high-risk conditions [4,5,9]. This limitation presents the urgent need for non-invasive, continuous sensing paradigms that can operate safely without bulky hardware or external electrical bias.

The persistence of this challenge is rooted in the fundamental physics of signal transduction. In most sensing architectures, conversion of a biological stimulus into a measurable output requires an externally imposed energy bias, typically in the form of applied voltages or driven currents [10-12]. While effective, such approaches introduce risks of electrical leakage, Joule heating, and electromagnetic interference concerns that become increasingly significant in soft, electrically sensitive tissues [13-15]. In the context of functional imaging, which aims to map dynamic physiological states rather than static anatomy, electrode-based systems further suffer from wiring density, packaging constraints, and limited spatial scalability, collectively referred to as the “wiring bottleneck” [16-17]. Although wearable and flexible sensors have advanced rapidly, most still rely on batteries or external biasing circuitry that complicate long-term deployment and compromise true non-invasiveness [18-22].

Previous attempts to circumvent these limitations have explored mechano-based transduction mechanisms, including mechanoluminescence and conventional piezophotonic effects, in which mechanical stress is converted directly into optical emission using non-centrosymmetric inorganic materials [10,23-24]. While these approaches have demonstrated strong signal generation and robustness in structural monitoring and energy-harvesting contexts, their operation typically relies on relatively large strain amplitudes, impact forces, or externally driven excitation that exceed the subtle mechanical signatures associated with physiological motion such as vascular pulsation, tissue micromechanics, or fetal cardiac activity [25-26]. Fluorescence-based molecular sensors, by contrast, offer high sensitivity and chemical specificity but generally lack intrinsic mechanisms for tunable electrostatic or dielectric modulation unless driven by externally applied electric fields or biasing circuitry [27-28]. As a result, despite advances in wearable mechano-transductive sensing and battery-free epidermal electronics, a critical gap remains for a biocompatible, molecular-scale interfacial system capable of converting ultra-low mechanical excitation into field-encoded optical contrast without external bias or high-stress activation [18,19,21].

In this work, we propose and theoretically develop a new interfacial paradigm to bridge this gap through the identification of a piezophotonic-induced Stark effect (PISE) at an excited-state intramolecular proton transfer (ESIPT) active organic-semi-conductor hybrid interface. Our approach develops a Quantum-Mechanical framework to explore the PISE using Luteolin–Polydopamine–BaTiO₃ hybrid interface as a representative material composite. In the PISE mechanism, coupled piezoelectric and photonic excitations generate localized electrostatic fields at hybrid interfaces without external bias. The central hypothesis is that the internal piezoelectric field generated within Barium Titanate (BaTiO₃) under low-frequency mechanical stimulation can be harnessed to modulate the excited-state intramolecular proton transfer (ESIPT) process of surface-anchored luteolin molecules. BaTiO₃ is a well-established piezoelectric material capable of generating substantial internal fields under modest mechanical deformation, even in flexible and thin-film configurations [29-32]. Luteolin(3',4',5,7-tetrahydroxyflavone), a naturally occurring flavonoid, is known to undergo ESIPT-mediated excited-state dynamics that are highly sensitive to local electric fields, providing an intrinsic optical reporter of electrostatic perturbations [33-38]. Polydopamine serves as a dielectric and chemical interlayer, enabling stable immobilization of luteolin while preserving

interfacial field coupling and molecular photophysics [39-42] and has been shown to enhance performance in piezoelectric nanocomposites [43-44].

The scope of this study is confined to the theoretical formulation and interfacial modeling of this bias-free sensing paradigm, with emphasis on the spectral Stark modulation of luteolin emission under low-amplitude mechanical excitation. The analysis focuses on surface-level and interface-mediated functional sensing rather than deep-tissue or volumetric structural imaging. While experimental realization and device integration remain beyond the present scope, the framework establishes a new class of energy-autonomous hybrid interfaces capable of translating benign mechanical stimuli into optically readable electrostatic contrast. If validated, this mechanism would provide a foundational pathway toward next-generation functional imaging and sensing platforms that operate without external bias, batteries, or invasive electrodes, complementing emerging trends in battery-free and mechanically driven biomedical sensors

2.0. THEORETICAL DERIVATION OF THE PISE MECHANISM

2.1. PISE Mechanism and Model Description

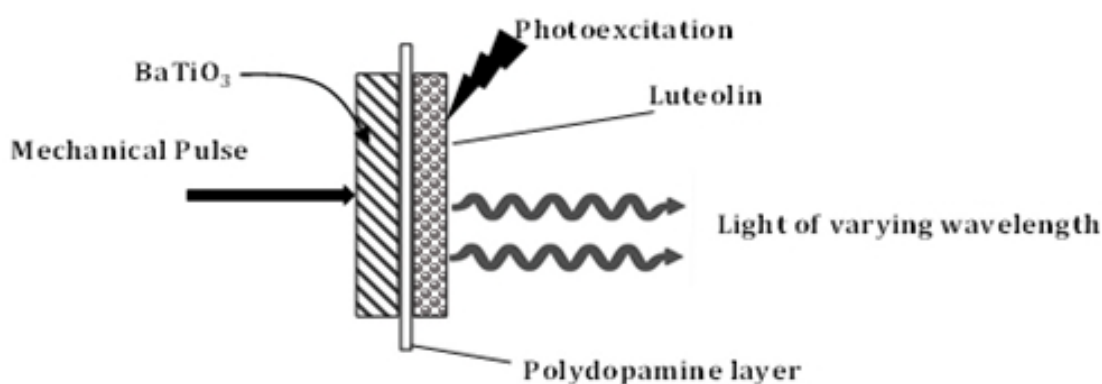


Figure 1a| Schematic illustration of the piezophotonic-induced Stark effect (PISE) at the Luteolin–Polydopamine–BaTiO₃ hybrid interface

The piezophotonic-induced Stark effect (PISE) at the Luteolin@Polydopamine–BaTiO₃ hybrid interface proceeds through a four-stage energy-transduction pathway that converts mechanical excitation into optically readable spectral modulation. As illustrated schematically in figure 1, an externally applied mechanical stimulus (e.g., pressure, pulse, or vibration) induces elastic deformation of the non-centrosymmetric BaTiO₃ lattice. This deformation results in relative displacement of the Ti⁴⁺ cations with respect to the O²⁻ anions, generating a net piezoelectric polarization and an associated surface piezopotential, Φ_{piezo} . At the nanoscale, even small lattice distortions can give rise to intense local electric fields, E_{piezo} , which may exceed 10^6 V m^{-1} at the BaTiO₃ surface. This piezoelectrically generated field is not confined to the ceramic phase but extends outward across the interface into the adjacent polydopamine (PDA) layer. Because the PDA coating is engineered to be ultrathin (typically $\sim 2\text{--}5 \text{ nm}$), attenuation of the electric field is minimal, allowing surface-anchored luteolin molecules to experience a substantial fraction of the interfacial field intensity.

Upon optical excitation, luteolin undergoes excited-state intramolecular proton transfer (ESIPT), evolving from the enol excited state (E^*) to the keto excited state (K^*). This process is accompanied by a pronounced redistribution of electronic charge and a large change in the molecular dipole moment ($\Delta\mu$). The interfacial piezoelectric field E_{piezo} interacts directly with this transition dipole, giving rise to a Stark perturbation of the excited-state energy levels. Physically, the applied field tilts the proton-transfer

potential energy surface, modifying the relative stabilization of the K^* state and altering the energy gap between the excited and ground states.

The cumulative effect of this electromechanical–photonic coupling is expressed as a field-dependent modulation of luteolin fluorescence. Rather than emitting at a fixed wavelength, the ESIPT-mediated emission exhibits shift in spectral position and/or intensity that scale with the magnitude of the mechanically induced piezoelectric field. Consequently, mechanical stimuli applied to the BaTiO_3 phase are transduced, without external electrical bias, into optically detectable signals via interfacial Stark modulation of molecular excited-state dynamics.

Figure 1(b) presents this mechanism and interfacial Physics in schematics

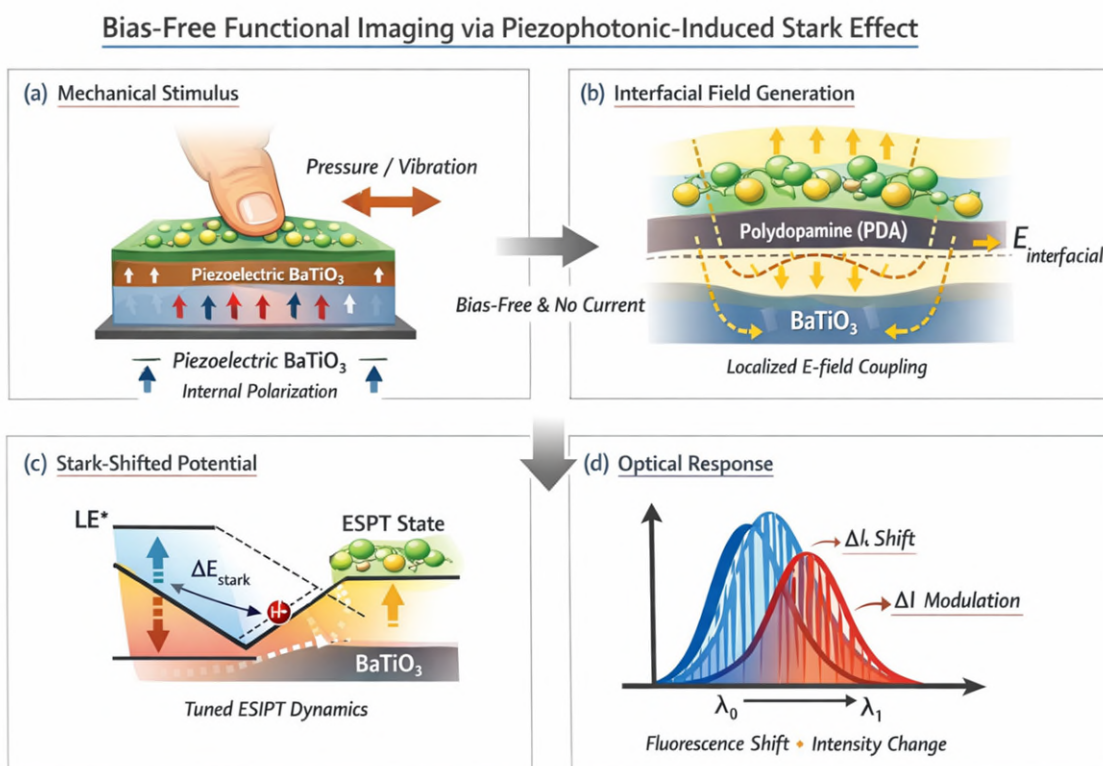


Figure 1(b). Piezophotonic-Induced Stark Effect (PISE) mechanism.

(a) Mechanical stress applied to BaTiO_3 generates piezoelectric polarization under open-circuit, bias-free conditions. (b) The resulting quasi-static electric field extends across the thin polydopamine (PDA) layer and couples electrostatically to surface-anchored luteolin molecules without current flow. (c) The interfacial field Stark-tilts the ESIPT excited-state potential of luteolin, shifting the emissive keto state via dipole–field interaction. (d) This modulation produces measurable optical readouts, observed as fluorescence wavelength shifts ($\Delta\lambda$) and/or intensity changes (ΔI), enabling bias-free mechanical sensing.

Polydopamine as a Dielectric and Orientational Bridge

Efficient operation of the piezophotonic-induced Stark effect requires precise molecular anchoring that preserves ESIPT photophysics while maximizing interfacial field coupling, a role fulfilled by polydopamine (PDA) as a dielectric bridge between luteolin and BaTiO_3 . PDA adheres robustly to oxide surfaces through catechol- and amine-mediated covalent and non-covalent interactions, providing mechanically stable coatings resistant to delamination under strain [39,41]. Its dense network of hydroxyl and amine groups

promotes directional hydrogen bonding with the phenolic hydroxyls of luteolin, constraining molecular orientation such that the ESIPT axis and associated transition dipole moment align approximately parallel to the interfacial piezoelectric field E_{piezo} , thereby maximizing Stark coupling $\Delta E_{\text{Stark}} \propto -\Delta\mu \cdot E_{\text{piezo}}$ [28,35]. Simultaneously, PDA acts as an electronic insulator, suppressing non-radiative quenching pathways that would arise from direct molecular contact with the BaTiO₃ lattice. When confined to thicknesses of $\sim 2 - 5 \text{ nm}$ with a dielectric constant $\epsilon_{\text{PDA}} \approx 3-5$, PDA preserves strong electrostatic field transmission while maintaining high fluorescence efficiency, enabling Stark-modulated ESIPT emission under mechanically generated fields approaching 10^6 V m^{-1} [43,44,45].

The feasibility of the PISE mechanism is anchored on the physical parameters of the materials in the interface. These parameters are summarized in Table 1

Table 1: Key Physical Parameters Governing the PISE Mechanism

Parameter	Symbol	Physical Role	Representative Value / Material
Piezoelectric coefficient	d_{33}	Determines magnitude of mechanically generated polarization and interfacial electric field	$\approx 190 \text{ pC N}^{-1}$ (BaTiO ₃)
ESIPT dipole change	$\Delta\mu$	Sets Stark sensitivity of the optical reporter via excited-state charge redistribution	High ($\approx 5-15 \text{ D}$, luteolin keto form)
Dielectric constant (interlayer)	ϵ_{PDA}	Controls electrostatic field transmission across the organic spacer	$\approx 5-10$ (polydopamine)
Interfacial spacing (anchoring distance)	d	Balances field strength retention against fluorescence quenching	$2-5 \text{ nm}$ (PDA layer thickness)
BaTiO ₃ surface field	E_{piezo}	Electrostatic driving force	up to 10^6 V m^{-1}
Orientation factor	$\langle \cos \theta \rangle$	Maximizes Stark interaction	$\rightarrow 1$ (aligned)

2.2. TENSOR ANALYSIS OF MECHANO-ELECTRIC TRANSDUCTION IN BATiO₃

The conversion of mechanical stress to an intrinsic electric field in barium titanate (BaTiO₃) is governed by the piezoelectric constitutive equations. For a rigorous treatment, we employ the tensorial formulation that naturally emerges from crystal symmetry and continuum mechanics.

The coupled electromechanical response of a piezoelectric material is described by the linear constitutive equations. In the *strain-charge* form, suitable for stress-driven systems, they are (Einstein summation implied):

$$\begin{aligned} \epsilon_{ij} &= s_{ijkl}^E \sigma_{kl} + d_{kij} E_k, \\ D_i &= d_{ikl} \sigma_{kl} + \epsilon_{ij}^\sigma E_j, \end{aligned} \quad (1)$$

Where ϵ_{ij} and σ_{kl} are the second-rank strain and stress tensors, respectively, E_k and D_i are the electric field and electric displacement vectors, s_{ijkl}^E is the fourth-rank elastic compliance tensor at constant electric field. d_{ikl} is the third-rank piezoelectric strain tensor and ϵ_{ij}^σ is the second-rank permittivity tensor at constant stress.

Equation (1) represents the standard linear constitutive framework of piezoelectricity, derived from thermodynamic potentials and validated across transducer physics and ferroelectric materials science[46,47].

We define the piezoelectric polarization P_i by the macroscopic Maxwell relation

$$D_i = \epsilon_{ij}^\sigma E_j + P_i \quad (2)$$

Comparing Eq. (1) and Eq. (2), the stress-induced polarization is

$$P_i(\sigma) = d_{ikl} \sigma_{kl} \quad (3)$$

Equation (3) is a tensorially exact statement of stress-to-polarization conversion for a linear piezoelectric material.

This formulation follows the standard linear treatment of piezoelectricity, which couples elastic and dielectric variables via the piezoelectric strain tensor. The constitutive relations in Eq. (1) are justified by the canonical description established in the IEEE Standard on Piezoelectricity and are derived from thermodynamic potentials in foundational texts on piezoelectric materials [46-47].

Voigt reduction and full matrix form for tetragonal BaTiO₃ (4mm)

At room temperature, BaTiO₃ possesses a non-centrosymmetric tetragonal $P4mm$ symmetry (point group $4mm$)[49,50].

In Voigt notation,

$$(1,2,3,4,5,6) \leftrightarrow (xx, yy, zz, yz, zx, xy), \sigma_\alpha = \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix} \quad (4a)$$

The non-zero, independent components of piezoelectric coefficients (d_{ijk}) are: $d_{33}, d_{31} = d_{32}, d_{15} = d_{24}$

Thus, the stress–polarization map (Eq. (3)) becomes the full Voigt matrix relation;

$$\begin{bmatrix} P_1 \\ P_2 \\ P_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \quad (4b)$$

For aligned uniaxial loading along the polar axis, $\sigma_3 = \sigma_{zz} \neq 0$ with other components negligible, Eq. (4b) reduces to

$$P_3 = d_{33}\sigma_{zz}, P_1 = P_2 = 0 \quad (5)$$

For BaTiO₃ domain is rotated relative to the laboratory frame, the tensor transforms as

$$d'_{ijk} = a_{ip}a_{jq}a_{kr}d_{pqr}, P_i = d'_{ikl}\sigma_{kl} \quad (6)$$

with a_{ip} the direction cosines; Eq. (6) is the rigorous route for orientation distributions.

The formulation here (Eqs.(1-6)) follow directly from the standard tensorial piezoelectric formalism established in classical transducer theory and codified in the IEEE piezoelectric standard [46,47]. The symmetry-reduced Voigt representation employed here is rigorously justified by the crystallographic point group of tetragonal BaTiO₃ [48-49]. The resulting stress-induced polarization generates internal electrostatic fields whose magnitude and nanoscale relevance are consistent with contemporary piezophotonic studies and BaTiO₃ nanophotonic systems [50-51].

Maxwell electrostatics and Gauss-law boundary conditions (bias-free)

The piezoelectrically induced polarization acts as a bound-charge source for the electric field. In the quasi-static regime relevant to physiological loading (low frequency, negligible magnetic induction), Maxwell's equations reduce to

$$\nabla \times \mathbf{E} = \mathbf{0} \Rightarrow \mathbf{E} = -\nabla\phi, \quad (7)$$

$$\nabla \cdot \mathbf{D} = \rho_f, \rho_f = 0 \text{ (no free charge; electrically isolated/open circuit)} \quad (8)$$

These relations constitute the electrostatic limit of Maxwell's equations in polarized media[52].

With $\mathbf{D} = \epsilon\mathbf{E} + \mathbf{P}$ inside BaTiO₃, and $\mathbf{D} = \epsilon_{\text{PDA}}\mathbf{E}$ in the PDA layer, Eq. (8) yields the governing electrostatic boundary-value problem

$$\nabla \cdot (\epsilon(\mathbf{r})\nabla\phi(\mathbf{r})) = \nabla \cdot \mathbf{P}(\mathbf{r}), \mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r}) \quad (9)$$

together with interface conditions at the BaTiO₃/PDA boundary (no free surface charge),

$$\hat{\mathbf{n}} \cdot (\mathbf{D}_{\text{in}} - \mathbf{D}_{\text{out}}) = 0, \phi_{\text{in}} = \phi_{\text{out}} \text{ (equivalently } \hat{\mathbf{n}} \times (\mathbf{E}_{\text{in}} - \mathbf{E}_{\text{out}}) = \mathbf{0}) \quad (10)$$

Equations (7)–(10) are the rigorous Maxwell closure (valid in the quasi-static limit [52–55]) required to convert $P(\sigma)$ into a physical field $\mathbf{E}$ in the PDA layer.

Closed-form field in the PDA layer for a uniformly polarized BaTiO₃ nanoparticle

To obtain an analytic expression, we model a single BaTiO₃ nanoparticle as a sphere of radius R embedded in PDA, with uniform polarization $\mathbf{P} = P\hat{\mathbf{z}}$ inside the particle (with P given by Eq. (4)–(6)). Let ϵ_1 denote the effective permittivity inside BaTiO₃ along the relevant direction, and $\epsilon_2 = \epsilon_{\text{PDA}} = \epsilon_0\epsilon_r$ the PDA permittivity.

Because $\nabla \cdot \mathbf{P} = 0$ in the bulk for uniform $\mathbf{P}$, the source appears as a bound surface charge $\sigma_b = \mathbf{P} \cdot \hat{\mathbf{n}} = P\cos\theta$ at $r = R$. The potentials satisfy Laplace's equation inside/outside with dipolar symmetry, so we take

$$\phi_{\text{in}}(r, \theta) = -A r \cos\theta, \phi_{\text{out}}(r, \theta) = \frac{B \cos\theta}{r^2}, (r > R) \quad (11)$$

Applying continuity of potential ϕ at $r = R$ gives $B = -AR^3$.

Applying continuity of normal displacement (Eq. (10)) with

$$\mathbf{D}_{\text{in}} = \epsilon_1 \mathbf{E}_{\text{in}} + \mathbf{P}, \mathbf{D}_{\text{out}} = \epsilon_2 \mathbf{E}_{\text{out}}, \quad (12)$$

yields

$$\epsilon_2 E_r^{\text{out}}(R, \theta) = \epsilon_1 E_r^{\text{in}}(R, \theta) + P \cos\theta \quad (13)$$

From $\mathbf{E} = -\nabla\phi$,

$$E_r^{\text{in}} = A \cos\theta, E_r^{\text{out}} = \frac{2B \cos\theta}{r^3} \quad (14)$$

Using $B = -AR^3$ in Eq. (14) gives

$$\epsilon_2(-2A \cos\theta) = \epsilon_1(A \cos\theta) + P \cos\theta \Rightarrow A = -\frac{P}{\epsilon_1 + 2\epsilon_2} \quad (15)$$

Therefore,

$$B = \frac{PR^3}{\epsilon_1 + 2\epsilon_2}, \phi_{\text{out}}(r, \theta) = \frac{PR^3}{\epsilon_1 + 2\epsilon_2} \frac{\cos\theta}{r^2} \quad (16)$$

Comparing Eq. (16) with the standard dipole potential in a dielectric,

$$\phi_{\text{dip}}(r, \theta) = \frac{1}{4\pi\epsilon_2} \frac{p_{\text{eff}} \cos \theta}{r^2} \quad (17)$$

identifies the effective dipole moment

$$p_{\text{eff}} = \frac{4\pi\epsilon_2 R^3}{\epsilon_1 + 2\epsilon_2} P \quad (18)$$

Hence, the full external electric field in PDA (for $r > R$) is the dipole field

$$E_m(\mathbf{r}) = \frac{1}{4\pi\epsilon_2} \left(\frac{3r_m r_n - r^2 \delta_{mn}}{r^5} \right) p_{\text{eff},n}, \epsilon_2 = \epsilon_0 \epsilon_r, \quad (19)$$

with $p_{\text{eff},n}$ given by Eq. (18) and P_n obtained tensorially from Eq. (3)/(6)/(8).

For a luteolin molecule located near the particle surface along the polarization axis ($\theta = 0$) at $r \simeq R + \delta$ with $\delta \ll R$, the field reduces to the on-axis component:

$$E_{\parallel}(r) = \frac{1}{4\pi\epsilon_2} \frac{2p_{\text{eff}}}{r^3} \simeq \frac{2}{\epsilon_1 + 2\epsilon_2} P \left(\frac{R}{R + \delta} \right)^3 \quad (20)$$

Using the aligned uniaxial case $P = d_{33}\sigma_{zz}$ from Eq. (5), the interfacial field becomes:

$$E_{\parallel}(R + \delta) \simeq \frac{2}{\epsilon_1 + 2\epsilon_2} d_{33}\sigma_{zz} \left(\frac{R}{R + \delta} \right)^3 \quad (21)$$

Equations (19)–(21) are the rigorous Maxwell-consistent field in the PDA layer generated by stress-induced polarization in BaTiO₃, including dielectric-contrast screening via $(\epsilon_1 + 2\epsilon_2)^{-1}$. This $E(\mathbf{r})$ is the field that enters the Stark interaction term in the molecular Hamiltonian of the luteolin chromophore.

Using the near-surface on-axis result in Eq.(21) we select representative values appropriate for BaTiO₃ nanoparticles coated by an ultrathin PDA interlayer: $d_{33} = 150 \text{ pC N}^{-1} = 1.50 \times 10^{-10} \text{ C N}^{-1}$, $\epsilon_1 = \epsilon_0 \epsilon_{r1}$ with $\epsilon_{r1} = 300$ (size-reduced effective permittivity typical of nanoscale BaTiO₃), $\epsilon_2 = \epsilon_0 \epsilon_{r2}$ with $\epsilon_{r2} = 4$ (polymer-like PDA), $R = 50 \text{ nm}$, and $\delta = 3 \text{ nm}$. For a representative low-amplitude mechanical loading $\sigma_{zz} = 1 \text{ kPa} = 10^3 \text{ Pa}$,

$$\epsilon_1 + 2\epsilon_2 = \epsilon_0(\epsilon_{r1} + 2\epsilon_{r2}) = \epsilon_0(300 + 8) = 308 \epsilon_0,$$

and

$$\left(\frac{R}{R + \delta} \right)^3 = \left(\frac{50}{53} \right)^3 \simeq 0.84.$$

Therefore,

$$E_{\parallel} \simeq \frac{2}{308 \epsilon_0} (1.50 \times 10^{-10})(10^3)(0.84) \approx 9.2 \times 10^1 \text{ V m}^{-1}.$$

Thus, kPa-scale loading yields $E_{\parallel} \sim 10^2 \text{ V m}^{-1}$ at the PDA outer surface under conservative dielectric screening.

Because Eq. (21) is linear in σ_{zz} under the assumed small-signal linear piezoelectric regime, the interfacial field scales as

$$E_{\parallel}(R + \delta) \approx (9.2 \times 10^{-2} \text{ V m}^{-1} \text{ Pa}^{-1}) \sigma_{zz}, (\text{for the parameter set above}).$$

Hence, the estimate interpolates directly across loading regimes:

$$\begin{aligned} \sigma_{zz} = 10^3 \text{ Pa} &\Rightarrow E_{\parallel} \approx 9.2 \times 10^1 \text{ V m}^{-1}, \\ \sigma_{zz} = 10^5 \text{ Pa} = 0.1 \text{ MPa} &\Rightarrow E_{\parallel} \approx 9.2 \times 10^3 \text{ V m}^{-1}, \\ \sigma_{zz} = 10^6 \text{ Pa} = 1 \text{ MPa} &\Rightarrow E_{\parallel} \approx 9.2 \times 10^4 \text{ V m}^{-1}. \end{aligned}$$

This scaling justifies extrapolating from physiological micro-pressures to ultrasound-driven stresses within the same formalism, provided the BaTiO₃ response remains within its linear electromechanical regime

and the effective nanoscale permittivity and domain configuration are appropriately characterized (since $E_{\parallel} \propto (\epsilon_1 + 2\epsilon_2)^{-1}$). In practice, local-field enhancement can exceed the spherical-on-axis estimate due to non-spherical particle shapes, domain inhomogeneity, and edge/fringing fields; therefore Eq. (21) should be interpreted as a conservative baseline for the near-field transmitted into the PDA layer.

2.3 Hilbert Space and Hamiltonian Formulation (PISE at Luteolin–PDA–BaTiO₃)

The Luteolin–Polydopamine–BaTiO₃ hybrid interface constitutes a multiscale system in which mechanical and electrostatic degrees of freedom are classical, while molecular excited-state dynamics are quantum mechanical. Following the derivation in Section 2.2, the mechanically induced piezoelectric polarization in BaTiO₃ generates a quasi-static interfacial electric field E_{int} , transmitted through the dielectric polydopamine (PDA) layer and experienced locally by surface-anchored luteolin molecules.

Accordingly, the total system is partitioned as Classical sector consisting of the Mechanical stress σ , piezoelectric polarization P , and electrostatic field E_{int} , governed by continuum piezoelectricity and Maxwell electrostatics (Section 2.2) and Quantum sector consisting of the electronic and nuclear degrees of freedom of the luteolin chromophore undergoing excited-state intramolecular proton transfer (ESIPT).

Composite Hilbert space and reduced electronic manifold

We model the PISE-active hybrid interface as a composite quantum system consisting of the luteolin chromophore (electrons + nuclei), the electromechanical BaTiO₃ transducer (treated as a quasi-static classical field source under low-frequency loading), and the polydopamine (PDA) dielectric interlayer and surrounding medium (treated as a dielectric environment that transmits and screens the field).

The full quantum state is defined on a complex, separable Hilbert space

$$\mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{mol}} \otimes \mathcal{H}_{\text{env}} \quad (22a)$$

where the molecular sector decomposes into electronic and nuclear subspaces,

$$\mathcal{H}_{\text{mol}} = \mathcal{H}_{\text{el}} \otimes \mathcal{H}_{\text{nuc}} \quad (22b)$$

We treat the interfacial chromophore (luteolin) as a quantum subsystem embedded in a quasi-static electrostatic environment generated by mechanically biased BaTiO₃ and transmitted through a thin PDA interlayer.

The full state space is written as

$$\mathcal{H} = \mathcal{H}_{\text{el}} \otimes \mathcal{H}_{\text{nuc}} \otimes \mathcal{H}_{\text{env}} \quad (22c)$$

Here $\mathcal{H}_{\text{el}}$ supports the electronic eigenmanifold of luteolin (in the presence of the interface), while $\mathcal{H}_{\text{nuc}}$ supports the nuclear coordinates $\mathbf{R}$ including the ESIPT proton-transfer coordinate and other vibrational modes that govern ultrafast relaxation and dual-channel emission in ESIPT dyes. $\mathcal{H}_{\text{env}}$ represents the classical electrostatic environment generated by the piezoelectric nanoparticle and the dielectric PDA interlayer.

This separation follows the standard molecular quantum framework and the Born–Oppenheimer partitioning used for excited-state proton-transfer systems [56–58]. The separation into electronic and nuclear subspaces reflects the established ESIPT modeling paradigm, where ultrafast emission commonly proceeds through a keto excited-state channel and can be captured by a reduced emissive manifold coupled to a small set of dominant nuclear coordinates[58,59–60]. The environmental sector $\mathcal{H}_{\text{env}}$ includes BaTiO₃ polarization and the PDA spacer because these control local field transmission and screening; PDA is widely established as a robust interfacial coating layer and has been explicitly used to engineer BaTiO₃ interfacial electromechanical behavior[39,61].

Since the experimentally relevant emission channel is the ESIPT-stabilized keto branch, we restrict the electronic sector to the reduced two-level subspace

$$\mathcal{H}_{\text{el}} = \text{span}\{|K_0\rangle, |K^*\rangle\} \quad (22d)$$

with $|K^*\rangle$ the emissive keto excited state and $|K_0\rangle$ its ground counterpart. The ESIPT coordinate is represented by a collective proton-transfer coordinate z (defined along the dominant intramolecular H-bond axis), with conjugate momentum $\hat{p}_z$.

Hamiltonian Formulation of PISE at the Luteolin@PDA–BaTiO₃ Interface

The effective Hamiltonian governing the ESIPT-active chromophore in the interfacial field is decomposed as

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{Stark}} + \hat{H}_{\text{env}} \quad (23)$$

where the three terms represent, respectively, the intrinsic molecular degrees of freedom, the electrostatic environment, and the molecule–field coupling.

This decomposition follows the standard structure used in excited-state embedding theory, quantum-confined Stark effect (QCSE) models, and polarizable environment treatments, in which the chromophore is treated quantum mechanically and the surrounding medium enters through electrostatic fields or reaction-field operators[52,57].

The molecular Hamiltonian is written as

$$\hat{H}_{\text{mol}} = \hat{T}_{\text{nuc}} + \hat{H}_{\text{el}}(\mathbf{R}), \quad (24)$$

where $\hat{T}_{\text{nuc}}$ is the nuclear kinetic energy operator and $\hat{H}_{\text{el}}(\mathbf{R})$ is the electronic Hamiltonian parametrically dependent on nuclear coordinates $\mathbf{R}$.

For ESIPT-active flavonoids such as luteolin, extensive experimental and theoretical studies demonstrate that optical emission is dominated by the keto excited-state channel $\{|K_0\rangle, |K^*\rangle\}$, reached after ultrafast intramolecular proton transfer [34,35,37]. Accordingly, the electronic Hilbert space is projected onto the emissive keto manifold without loss of physical content for spectroscopy-based observables. Within this reduced manifold, the relevant electronic redistribution occurs predominantly along the direction normal to the interface z . This reduced description is standard in ESIPT theory and fluorescence sensing, where higher electronic states and non-emissive intermediates are integrated out into effective potentials and linewidths [59].

Introducing an effective one-dimensional electronic coordinate z , the molecular Hamiltonian reduces to

$$\hat{H}_{\text{mol}} = -\frac{\hbar^2}{2m^*} \frac{d^2}{dz^2} + V(z; E_{\text{ff}}) \quad (25)$$

where m^* is an effective electronic mass and $V(z; E_{\text{eff}})$ is the field-dependent molecular potential.

We model the intrinsic spatial extent of the emissive electronic density normal to the interface by a finite confinement region of width L . In the absence of an external field, this is represented by

$$V_0(z) = \begin{cases} 0, & 0 \leq z \leq L, \\ \infty, & \text{otherwise.} \end{cases} \quad (26)$$

The mechanically generated interfacial field produces a Stark perturbation via the dipole–field interaction. Projected onto the effective coordinate z , this yields a linear potential contribution $eE_{\text{eff}}z$ within the confinement region. The resulting field-modified molecular potential is therefore

$$V(z; E_{\text{eff}}) = \begin{cases} eE_{\text{eff}}z, & 0 \leq z \leq L, \\ \infty, & \text{otherwise.} \end{cases} \quad (27)$$

Equations (25)–(27) define a slanted (triangular) infinite well, which constitutes the standard Hamiltonian underlying quantum-confined Stark effect (QCSE) analyses in confined electronic systems.

The environment term $\hat{H}_{\text{env}}$ collects vibrational bath and dielectric polarization contributions; for the present spectral-shift derivation we do not require an explicit bath model and retain $\hat{H}_{\text{env}}$ only as the source of dephasing and linewidth broadening (treated later in the TDSE/open-system section).

Stark interaction induced by the piezoelectric field

The PISE mechanism enters through the interfacial electric field produced by stress-induced polarization in BaTiO₃ and transmitted into PDA. In the quasi-static regime (physiological frequencies/ultrasound envelopes) the field is electrostatic, $\nabla \times \mathbf{E} = 0$, hence $\mathbf{E} = -\nabla\phi$. The resulting **local interfacial field** experienced by the anchored chromophore, $\mathbf{E}_{\text{loc}}(\mathbf{r})$, is obtained from the Maxwell/Gauss boundary-value solution derived in Section 2.2[42,43,52].

The dipole coupling is

$$\hat{H}_{\text{Stark}} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}_{\text{loc}} \quad (28a)$$

where $\hat{\boldsymbol{\mu}}$ is the molecular dipole operator. Projecting onto the emissive keto manifold yields a **state-dependent constant Stark shift**

$$\hat{H}_{\text{Stark}}^{(s)} = -\mu_s E_{\text{loc}}, s \in \{g, e\} \quad (28b)$$

with $\mu_s = \langle s | \hat{\boldsymbol{\mu}} | s \rangle$. The difference $\Delta\mu = \mu_e - \mu_g$ governs the molecular Stark shift of the optical transition[32,34].

Combining both contributions, the total Hamiltonian governing the excited-state proton dynamics reduces to the one-dimensional form.

Collecting terms, the effective one-dimensional Hamiltonian governing each electronic manifold sbecomes

$$\hat{H} = -\frac{\hbar^2}{2m_{\text{eff}}} \frac{d^2}{dz^2} + V(z; E_{\text{eff}}) - \mu_s E_{\text{loc}} \quad (29)$$

where the stress dependence enters exclusively through the local electric field $E_{\text{loc}}(\sigma)$, derived from piezoelectric constitutive relations under open-circuit (bias-free) boundary conditions.

This Hamiltonian makes explicit that mechanical stress modulates molecular excited-state energies purely via electrostatic coupling, without carrier injection, current flow, or external electrical bias—thereby defining the piezophotonic-induced Stark effect as a field-mediated, energy-autonomous transduction mechanism.

2.4 Time-Independent Schrödinger Equation and Field-Regime Analysis

From the field-dependent confinement potential in Eq. (27), the spectral properties of Eq. (29) are governed by the competition between kinetic confinement and the linear Stark tilt. The QCSE term in Eq. (29) (the first two terms) represents a particle in a tilted infinite well.

Within the well ($0 < z < L$), the linear potential is

$$eEz \quad (30)$$

The competition between quantum confinement and the Stark slope is governed by the dimensionless parameter

$$\eta \equiv \frac{eEL}{\mathcal{E}_1^{(0)}} \quad (31)$$

Where $\mathcal{E}_1^{(0)}$ is the field-free ground-state confinement energy

$$\mathcal{E}_1^{(0)} = \frac{\hbar^2 \pi^2}{2m_{\text{eff}} L^2} \quad (32)$$

Equation (29) admits two asymptotic regimes viz the Weak-field regime ($\eta \ll 1$) where the Stark term acts as a perturbation to the flat confinement and the Strong-field regime ($\eta \gtrsim 1$) where the potential tilt dominates, polarizing the eigenfunctions toward the interface.

The Hamiltonian itself is exact for all η ; only the solution strategy differs between regimes.

Weak-field regime ($\eta \ll 1$)

In the weak-field limit, Eq. (29) is decomposed as

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (33)$$

With

$$\hat{H}_0 = -\frac{\hbar^2}{2m_{\text{eff}}} \frac{d^2}{dz^2} + V_0(z), \hat{H}' = eE z, \quad (34)$$

and $V_0(z)$ the infinite square-well potential in Eq.(26).

with

$$V_0(z) = \begin{cases} 0, & 0 < z < L \\ \infty, & \text{otherwise} \end{cases}, \psi(0) = \psi(L) = 0.$$

Unperturbed eigenpairs:

$$\psi_n^{(0)}(z) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi z}{L}\right), \mathcal{E}_n^{(0)} = \frac{\hbar^2 \pi^2 n^2}{2m^* L^2} \quad (35)$$

Perturbative expansion:

$$\mathcal{E}_n(E_{\text{eff}}) = \mathcal{E}_n^{(0)} + \mathcal{E}_n^{(1)} + \mathcal{E}_n^{(2)} + O(E^3) \quad (36a)$$

with standard formulas

$$\mathcal{E}_n^{(1)} = \langle n | \hat{H}' | n \rangle, \mathcal{E}_n^{(2)} = \sum_{m \neq n} \frac{|\langle m | \hat{H}' | n \rangle|^2}{\mathcal{E}_n^{(0)} - \mathcal{E}_m^{(0)}} \quad (36b)$$

The First-order (linear Stark) shift is thus:

$$\mathcal{E}_n^{(1)} = eE \langle n | z | n \rangle = eE \int_0^L z |\psi_n^{(0)}(z)|^2 dz = eE \frac{L}{2} \quad (37)$$

This is independent of n (a known feature of the infinite well under a linear perturbation).

The Second-order correction (state-dependent term) is

For $m \neq n$,

$$\langle m | z | n \rangle = \frac{2}{L} \int_0^L z \sin \frac{m\pi z}{L} \sin \frac{n\pi z}{L} dz = \frac{4Lmn[(-1)^{m+n} - 1]}{\pi^2(m^2 - n^2)^2} \quad (38)$$

Thus, only opposite parity pairs contribute ($m + n$ odd).

Inserting $\hat{H}' = eEz$ into $\mathcal{E}_n^{(2)}$, using

$$\mathcal{E}_n^{(0)} - \mathcal{E}_m^{(0)} = \frac{\hbar^2 \pi^2}{2m^* L^2} (n^2 - m^2),$$

and perform the (convergent) series over $m \neq n$. The closed form becomes:

$$\mathcal{E}_n^{(2)} = (eE)^2 \frac{m^* L^4}{\hbar^2} \left(\frac{1}{24\pi^2 n^2} - \frac{5}{8\pi^4 n^4} \right) \quad (39)$$

This is the weak-field asymptotic corresponding to the Airy (triangular-well) problem, consistent with QCSE perturbative limits[63-64].

Combine $\mathcal{E}_n^{(0)}$, Eqs.(37) and (39):

$$\mathcal{E}_n(E) = \frac{\hbar^2 \pi^2 n^2}{2m^* L^2} + eE_{\text{eff}} \frac{L}{2} + (eE)^2 \frac{m^* L^4}{\hbar^2} \left(\frac{1}{24\pi^2 n^2} - \frac{5}{8\pi^4 n^4} \right) + O(E^3) \quad (40)$$

The first-order term is state-independent, so *transition energies* often depend mainly on the second-order (and higher) terms unless the two manifolds have different L and/or m^* .

Strong-Field Regime ($\eta \gtrsim 1$)

For fields such that $eEL \sim \mathcal{E}_1^{(0)}$, perturbation theory fails and Eq. (29) must be solved exactly.

Within $0 < z < L$, the TISE reads

$$\left[-\frac{\hbar^2}{2m_{\text{eff}}} \frac{d^2}{dz^2} + eE z \right] \psi(z) = \mathcal{E} \psi(z) \quad (41)$$

with boundary conditions $\psi(0) = \psi(L) = 0$.

Introducing the characteristic field length

$$\ell_E = \left(\frac{\hbar^2}{2m_{\text{eff}}(e - \Delta\mu)E} \right)^{1/3} \quad (42a)$$

and the scaled coordinate

$$\xi = \frac{z - \mathcal{E}/[(e - \Delta\mu)E]}{\ell_E} \quad (42b)$$

Eq. (41) reduces exactly to the Airy equation

$$\frac{d^2 \psi}{d\xi^2} - \xi \psi = 0 \quad (43)$$

Eq.(43) admits the general solution

$$\psi(z) = A \text{Ai}(\xi) + B \text{Bi}(\xi) \quad (44a)$$

Imposing $\psi(0) = 0$ and $\psi(L) = 0$, with

$$\xi_0 = \frac{-\mathcal{E}/(eE)}{\ell_E}, \xi_L = \frac{L - \mathcal{E}/(eE)}{\ell_E}$$

gives the homogeneous linear system

$$A \text{Ai}(\xi_0) + B \text{Bi}(\xi_0) = 0, \quad A \text{Ai}(\xi_L) + B \text{Bi}(\xi_L) = 0$$

A nontrivial solution exists only if the determinant vanishes:

$$\text{Ai}(\xi_0)\text{Bi}(\xi_L) - \text{Bi}(\xi_0)\text{Ai}(\xi_L) = 0 \quad (44b)$$

Eigenfunctions are normalized on $[0, L]$:

$$\int_0^L |\psi_n(z)|^2 dz = 1 \quad (44c)$$

Total Transition Energy and PISE Shift

The total energy of a state s is the sum of the QCSE eigenvalue and the dipole shift:

$$\mathcal{E}_{n,s}(E) = \mathcal{E}_n^{\text{Airy}}(E) - \mu_s E \quad (45)$$

The photonic transition energy between the excited keto state (K^* , with quantum number n) and the ground keto state (K_0 , with quantum number m) is therefore

$$h\nu(E) = \mathcal{E}_{n,K^*}(E) - \mathcal{E}_{m,K_0}(E) = [\mathcal{E}_n^{\text{Airy}}(E) - \mathcal{E}_m^{\text{Airy}}(E)] - \Delta\mu E, \quad (46)$$

where $\Delta\mu = \mu_{K^*} - \mu_{K_0}$. The Piezophotonic-Induced Stark Shift is defined as the change in this transition energy relative to the zero-field case:

$$\Delta\nu_{\text{PISE}}(E) = \frac{1}{h} [h\nu(E) - h\nu(0)] \quad (47)$$

For the interfacial fields and nanometer-scale confinement relevant to the Luteolin@PDA–BaTiO₃ system, the parameter η typically approaches or exceeds unity. Therefore, the system operates in or near the strong-field regime, necessitating the full Airy-function solution for quantitative predictions of the QCSE contribution. The weak-field expansion (Eq. 36) serves as a crucial consistency check in the limiting case of very small perturbations.

2.5 Photoexcitation-Driven Dynamics and Time-Dependent Schrödinger Equation (TDSE)

2.5.1 Field-dressed stationary basis

Let $s \in \{g, e\}$ denote the keto ground/excited manifolds $\{|K_0\rangle, |K^*\rangle\}$. For a fixed interfacial field F (quasi-static on electronic timescales), define the field-dressed eigenstates $\{|\phi_{n,s}(E)\rangle\}$ and eigenenergies $E_{n,s}(E)$ by

$$\hat{H}_s(E) |\phi_{n,s}(E)\rangle = E_{n,s}(E) |\phi_{n,s}(E)\rangle \quad (48)$$

With

$$\mathcal{E}_{n,s}(E) = \mathcal{E}_n^{\text{Airy}}(E) - \mu_s E \quad (49)$$

where $\mathcal{E}_n^{\text{Airy}}(E)$ is obtained from the Dirichlet Airy quantization condition and $-\mu_s E$ is the constant manifold Stark offset. This basis diagonalizes the static PISE Hamiltonian.

Total Time-Dependent Hamiltonian

Photoexcitation enters as a time-dependent dipole coupling to the optical electric field $\mathbf{E}_{\text{opt}}(t)$. The TD Hamiltonian is

$$\hat{H}(t; E) = \hat{H}_0(E) + \hat{H}_{\text{opt}}(t) \quad (50)$$

where $\hat{H}_0(E)$ is the field-dressed (PISE) Hamiltonian already derived (QCSE + dipole shift), and

$$\hat{H}_{\text{opt}}(t) = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}_{\text{opt}}(t) \quad (51)$$

For a linearly polarized excitation field along a unit vector $\hat{\mathbf{e}}$,

$$\mathbf{E}_{\text{opt}}(t) = \hat{\mathbf{e}} \mathcal{E}(t) \cos(\omega_L t + \varphi) \quad (52)$$

with envelope $\mathcal{E}(t)$, carrier frequency ω_L , and phase φ .

The wavefunction obeys

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t; F) |\Psi(t)\rangle \quad (53)$$

Expand in the field-dressed stationary basis:

$$|\Psi(t)\rangle = \sum_n c_{n,g}(t) |\phi_{n,g}(E)\rangle + \sum_n c_{n,e}(t) |\phi_{n,e}(E)\rangle \quad (54)$$

Insertion into Eq.(53) yields coupled amplitude equations

$$i\hbar \dot{c}_{n,s}(t) = \mathcal{E}_{n,s}(E) c_{n,s}(t) + \sum_{m,s'} V_{ns,ms'}^{\text{opt}}(t) c_{m,s'}(t) \quad (55)$$

with optical coupling matrix elements

$$V_{ns,ms'}^{\text{opt}}(t) = \langle \phi_{n,s}(E) | \hat{H}_{\text{opt}}(t) | \phi_{m,s'}(E) \rangle \quad (56)$$

Because $\hat{H}_{\text{opt}}$ is dipolar, the dominant couplings are inter-manifold ($g \leftrightarrow e$):

$$V_{ng,me}^{\text{opt}}(t) = -\boldsymbol{\mu}_{ng,me}(E) \cdot \mathbf{E}_{\text{opt}}(t), \boldsymbol{\mu}_{ng,me}(E) \equiv \langle \phi_{n,g}(E) | \hat{\boldsymbol{\mu}} | \phi_{m,e}(E) \rangle \quad (57)$$

Thus, photoexcitation enters the TDSE entirely through the dipole matrix element $\mu_{ng,me}(E)$ and the optical field $\mathbf{E}_{\text{opt}}(t)$. Importantly, $\mu_{ng,me}(E)$ is field-dependent because the Airy eigenfunctions are field-polarized, providing a direct mechanism for intensity modulation (field-dependent oscillator strength).

Two-level reduction (spectroscopy-relevant limit)

For narrowband excitation addressing a dominant transition (m, g) $\rightarrow$ (n, e), truncate to $\{|g\rangle, |e\rangle\} \equiv \{|\phi_{m,g}(E)\rangle, |\phi_{n,e}(E)\rangle\}$.

The TDSE becomes

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_g \\ c_e \end{pmatrix} = \begin{pmatrix} \mathcal{E}_g(E) & -\boldsymbol{\mu}_{ge}(E) \cdot \mathbf{E}_{\text{opt}}(t) \\ -\boldsymbol{\mu}_{eg}(E) \cdot \mathbf{E}_{\text{opt}}(t) & \mathcal{E}_e(E) \end{pmatrix} \begin{pmatrix} c_g \\ c_e \end{pmatrix} \quad (58)$$

Under near-resonant driving, slowly varying envelope, and $|\Omega| \ll \omega_L$, we apply the rotating-wave approximation. Transforming to the interaction picture and applying the rotating-wave approximation (RWA) yields

$$\dot{c}_e(t) = -\frac{i}{2} \Omega(F, t) e^{i\Delta(F)t} c_g(t), \dot{c}_g(t) = -\frac{i}{2} \Omega(F, t) e^{-i\Delta(F)t} c_e(t), \quad (59)$$

where the field-dependent detuning and Rabi frequency are

$$\Delta(F) = \omega_L - \frac{\mathcal{E}_e(E) - \mathcal{E}_g(E)}{\hbar} = \omega_L - 2\pi\nu(E) \quad (60a)$$

$$\Omega(F, t) = \frac{2}{\hbar} |\boldsymbol{\mu}_{ge}(F) \cdot \hat{\mathbf{e}}| \mathcal{E}(t) \quad (60b)$$

Here $\nu(F)$ is exactly the transition frequency derived from the Airy + dipole energies in Section 2.4, establishing the closed link:

Here, $\nu(E)$ is the piezoelectric-field-dependent transition frequency derived in Eq. (43). This establishes the closed link:

$$\sigma \xrightarrow{\text{piezo}} E(\sigma) \xrightarrow{\text{PISE}} \nu(E(\sigma)) \xrightarrow{\text{optics}} \text{spectral/intensity response.} \quad (61)$$

In the present dynamical formulation, excited-state intramolecular proton transfer (ESIPT) enters implicitly rather than as an explicit reaction coordinate. This treatment is justified by the well-established ultrafast ESIPT kinetics in flavonoid chromophores, which occur on sub-picosecond timescales and efficiently funnel population into the stabilized keto excited state prior to radiative decay. Consequently, optical emission is modeled exclusively within the emissive keto manifold $|K^*\rangle \rightarrow |K_0\rangle$, while non-

emissive intermediates are integrated out at the Hamiltonian level. The influence of ESIPT on the spectral response is retained through the intrinsic difference in permanent dipole moment between the keto excited and ground states, $\Delta\mu = \mu_{K^*} - \mu_{K_0}$, which contributes a state-dependent constant Stark offset to the total transition energy. Within this framework, the ultrafast ESIPT dynamics re-enter the theory only through the initial condition viz preparation of the keto excited-state population following photoexcitation and through the field-dependent transition parameters $\nu(E)$ and $\mu_{ge}(E)$ that govern the optical response. This separation of timescales is standard in contemporary ESIPT spectroscopy and sensing models, where proton transfer establishes the emissive manifold while subsequent electronic polarization and radiative dynamics encode external perturbations, enabling analytically tractable yet physically faithful descriptions of field-modulated emission[65-67].

2.6 Open-System Dynamics and Fluorescence Readout

The coherent TDSE describes photoexcitation and state evolution but does not account for spontaneous emission, nonradiative decay, or environmental dephasing—processes essential for modeling fluorescence intensity and lineshape. To connect the PISE theory to measurable observables, we extend the description to an open quantum system via the Lindblad master equation for the density operator $\hat{\rho}(t)$.

Master Equation for the Field-Dressed Two-Level System

For the two-level reduction $\{|g\rangle, |e\rangle\}$ defined in Section 2.5, the system's dynamics under incoherent processes are governed by:

$$\dot{\hat{\rho}}(t) = -\frac{i}{\hbar} [\hat{H}(t; F), \hat{\rho}(t)] + \mathcal{L}_{\text{rad}}[\hat{\rho}] + \mathcal{L}_{\text{deph}}[\hat{\rho}] \quad (62)$$

where the first term gives the coherent evolution from Eq. (54). The Lindblad dissipators are:

$$\mathcal{L}_{\text{rad}}[\hat{\rho}] = \Gamma_r \left(\hat{\sigma}_- \hat{\rho} \hat{\sigma}_+ - \frac{1}{2} \{ \hat{\sigma}_+ \hat{\sigma}_-, \hat{\rho} \} \right) \quad (63a)$$

$$\mathcal{L}_{\text{deph}}[\hat{\rho}] = \gamma_\phi (\hat{\sigma}_z \hat{\rho} \hat{\sigma}_z - \hat{\rho}) \quad (63b)$$

Here, $\hat{\sigma}_- = |g\rangle\langle e|$, $\hat{\sigma}_+ = \hat{\sigma}_-^\dagger$, $\hat{\sigma}_z = |e\rangle\langle e| - |g\rangle\langle g|$, Γ_r is the radiative decay rate (inverse of the fluorescence lifetime τ_{rad}), and γ_ϕ is the pure dephasing rate.

Steady-State Fluorescence Intensity and Spectrum

For continuous-wave (CW) optical excitation, the system reaches a steady state ($\dot{\hat{\rho}} = 0$). The steady-state excited-state population $\rho_{ee}^{\text{ss}}(E)$ and the fluorescence intensity $I_{\text{fl}}(E)$ the experimentally measured quantity becomes:

$$I_{\text{fl}}(F) \propto \Gamma_r \rho_{ee}^{\text{ss}}(E) \quad (64)$$

The population $\rho_{ee}^{\text{ss}}(F)$ depends on the field-dependent parameters $\nu(E)$ and $\mu_{ge}(E)$ through the optical Bloch equations derived from Eq. (59). In the weak-excitation limit ($\Omega \ll \Gamma_2$, with $\Gamma_2 = \Gamma_r/2 + \gamma_\phi$ the total dephasing rate), it simplifies to:

$$\rho_{ee}^{\text{ss}}(F) \approx \frac{|\Omega(E)|^2/4}{\Delta(F)^2 + \Gamma_2^2/4} \quad (65)$$

where $\Delta(F)$ and $\Omega(E)$ are given by Eqs. (60a) and (60b). The field-dependent fluorescence intensity therefore encodes the mechanical stimulus through two channels: the detuning $\Delta(F)$ and the transition dipole $\mu_{ge}(E)$ in $\Omega(E)$.

The steady-state emission spectrum, obtained via the Wiener-Khinchin theorem as the Fourier transform of the dipole autocorrelation function, is a Lorentzian centered at $\nu(E)$:

$$S(\omega; E) \propto \frac{\Gamma_r \rho_{ee}^{ss}(E)}{(\omega - 2\pi\nu(E))^2 + (\Gamma_2/2)^2} \quad (66)$$

The PISE spectral shift $\Delta\nu_{\text{PISE}} = \nu(E) - \nu(0)$ is thus directly observable as the peak displacement of $S(\omega; E)$.

Dynamic Sensing and Adiabatic Following

For a time-varying mechanical stress $\sigma(t)$ producing a field $F(t)$, the sensor operates in two regimes:

Adiabatic: If $F(t)$ varies slowly relative to Γ_2^{-1} , the spectrum adiabatically follows $S(\omega; F(t))$, and the peak tracks $\nu(F(t))$.

Non-Adiabatic: For faster modulation, the full time-dependent master equation (59) must be solved; the emitted light then carries phase information about $F(t)$.

This framework confirms that the Luteolin@PDA–BaTiO₃ interface operates as a fully passive, bias-free optomechanical transducer, converting mechanical energy into a modulated optical signal through the quantum-mechanically rigorous Piezophotonic-Induced Stark Effect.

2.7 Experimental Read-out and Model Outputs

The formulation developed above yields a direct mapping between mechanical excitation and experimentally accessible optical signals. The primary read-out is the field-dependent transition energy

$$h\nu(E) = [\mathcal{E}_{n,e}^{\text{Airy}}(E) - \mathcal{E}_{m,g}^{\text{Airy}}(E)] - \Delta\mu E_{\text{loc}},$$

from which the piezophotonic-induced Stark shift

$$\Delta\nu_{\text{PISE}} = \frac{1}{h} [h\nu(E) - h\nu(0)]$$

is obtained as the measurable spectral displacement of the fluorescence peak. Using the open-circuit piezoelectric relation $F_{\text{loc}} = F_{\text{loc}}(\sigma)$, this defines a closed, bias-free stress-to-frequency transduction law.

In addition to spectral shifts, the time-dependent formulation yields a field-dependent transition dipole moment $\mu_{ge}(E) = \langle \phi_g(E) | \hat{\mu} | \phi_e(E) \rangle$, reflecting polarization of the Airy eigenstates and leading to a concomitant modulation of emission intensity. For the interfacial fields and nanometer-scale confinement relevant to the Luteolin@PDA–BaTiO₃ system, the dimensionless parameter $\eta = eFL/\mathcal{E}_1^{(0)}$ approaches or exceeds unity, placing the system in the strong-field regime where the full Airy solution governs the observable response. Together, the spectral and intensity channels constitute the complete experimental output of the PISE mechanism.

2.8. RANGE OF VALIDITY AND APPLICATION WINDOW

The present model is valid for linear piezoelectric response $P_i = d_{ij}\sigma_j$ under quasi-static excitation $\omega_{\text{mech}} \ll c/R$, uniform nanoparticle polarization $20 \text{ nm} \lesssim R \lesssim 100 \text{ nm}$, dielectric field transmission $E_{\parallel} \propto R^3/(R + \delta)^3$ with $2 \text{ nm} \lesssim \delta \lesssim 5 \text{ nm}$, quantum confinement satisfying $\eta = eE_{\parallel}L/E_0 \lesssim \mathcal{O}(1)$, and optical readout governed by two-level Lorentzian response $I/I_0 = [1 + (\Delta\omega/\Gamma_2)^2]^{-1}$ for mechanical frequencies $\omega_{\text{mech}} \lesssim \Gamma_2$, yielding a bias-free mapping $\sigma \rightarrow E_{\parallel} \rightarrow \Delta E \rightarrow I/I_0$. Within this window, the piezophotonic-induced Stark mechanism yields a quantitatively reliable, bias-free mapping

$$\sigma \rightarrow E_{\parallel} \rightarrow \Delta E \rightarrow I/I_0.$$

3.0. RESULTS AND DISCUSSION

Here we present the analysis of the formulation in Eqs.(1)-(66). The parameters employed in the PISE model, along with their literature sources and computational roles, are summarized in Table 1. Conservative ranges were used to ensure robustness across expected material and physiological variations.

Figure 2 illustrates the mechanically induced generation of an interfacial electric field at the BaTiO₃–PDA interface, showing a linear increase of $E_{\text{interface}}$ with applied mechanical stress for different PDA spacer thicknesses (2–5 nm), thereby quantifying thickness-dependent field attenuation while preserving proportional stress–field transduction.

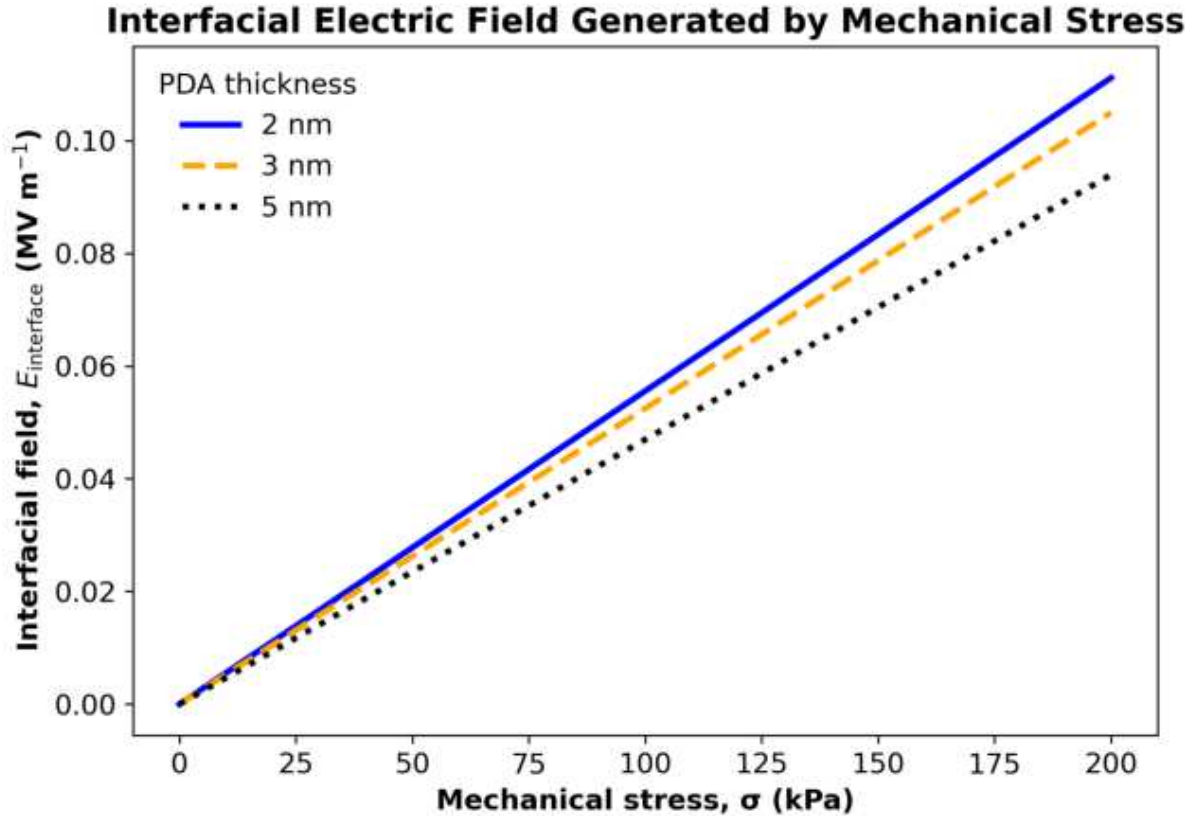


Figure 2: Stress–Field Transduction at the BaTiO₃–PDA Interface

Figure 2 shows a strictly linear increase of the interfacial electric field $E_{\text{interface}}$ with applied mechanical stress σ over the full investigated range (0–200 kPa), independent of PDA thickness. For a 2 nm PDA spacer, the interfacial field reaches $\sim 0.11 \text{ MV m}^{-1}$ at 200 kPa, decreasing systematically to $\sim 0.105 \text{ MV m}^{-1}$ and $\sim 0.09 \text{ MV m}^{-1}$ for spacer thicknesses of 3 nm and 5 nm, respectively. The slopes of the stress–field curves remain constant, indicating proportional transduction efficiency, while the vertical offset between curves quantifies thickness-dependent attenuation. Notably, even at moderate physiological–ultrasound stress levels (50–100 kPa), the predicted fields remain in the 10^4 – 10^5 V m^{-1} regime, sufficient to induce measurable Stark shifts in confined molecular systems.

The observed linearity arises directly from the piezoelectric constitutive relation $P = d_{33}\sigma$, which ensures that stress-induced polarization scales proportionally with applied load. The dependence on PDA thickness originates from electrostatic field transmission across the dielectric spacer, captured by the geometric attenuation factor $(R/(R + \delta))^3$ in the formulation. Increasing δ does not suppress field

generation at the BaTiO₃ core but reduces the effective field sampled at the molecular interface due to near-field decay. Importantly, the persistence of linearity across all thicknesses demonstrates that the PDA layer acts as a passive field modulator, not an active electromechanical element, preserving deterministic stress–field mapping while allowing independent control of interfacial photophysics.

Previous piezoelectric sensing studies predominantly report macroscopic voltages or currents extracted through electrodes, where interfacial electric fields are indirect, spatially averaged, and bias-dependent [68-69]. In contrast, the result provides a direct quantitative prediction of nanoscale interfacial fields generated purely by mechanical stress, without external bias or charge collection. Related piezoelectric heterostructure studies have shown that such local fields can drive interfacial electronic processes, particularly in catalysis and charge separation, but their role in optical Stark modulation has remained largely unexplored [70]. The result provides the foundational step of the thesis: mechanical deformation alone can generate a predictable, design-tunable interfacial electric field of sufficient magnitude to drive quantum-confined Stark modulation, enabling bias-free optical sensing and functional imaging in mechanically active environments.

Figure 3 presents the mechanical stress-induced interfacial field generation computed via the stress relations.

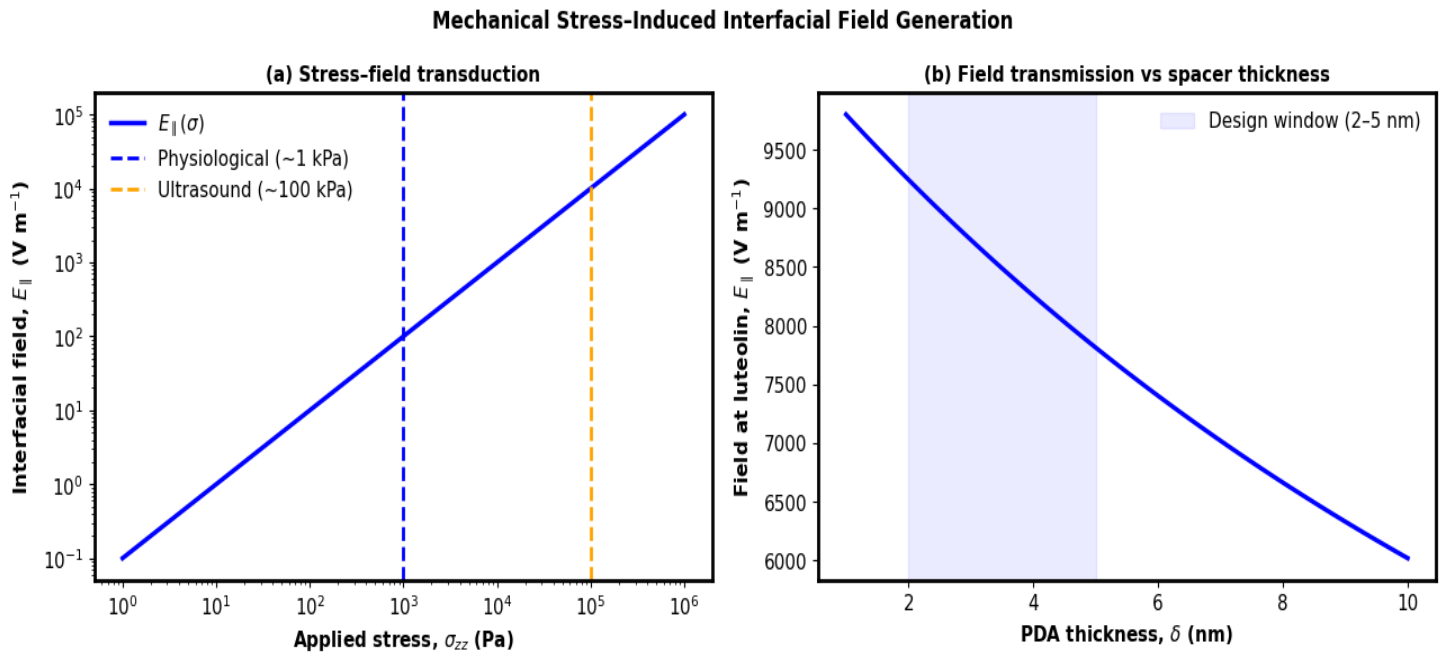


Figure 3| Stress–Field Transduction and Field Transmission at the BaTiO₃–PDA Interface

Figure 3a demonstrates a strictly linear relationship between the applied mechanical stress σ_{zz} and the interfacial electric field $E_{||}$ generated at the BaTiO₃–PDA interface over more than six orders of magnitude in stress (1 Pa–1 MPa). The log–log slope is unity, confirming proportional stress–field transduction. At physiologically relevant stresses (~ 1 kPa), the interfacial field reaches $\sim 10^2 \text{ V m}^{-1}$, increasing to $\sim 10^4 \text{ V m}^{-1}$ under ultrasound-scale loading (~ 100 kPa), and approaching $\sim 10^5 \text{ V m}^{-1}$ at higher stresses. Figure 3b shows the transmission of this field to the luteolin layer as a function of PDA thickness at fixed stress ($\sigma = 100$ kPa). The transmitted field decreases monotonically from $\sim 1.04 \times 10^4 \text{ V m}^{-1}$ at $\delta = 1 \text{ nm}$ to $\sim 6.4 \times 10^3 \text{ V m}^{-1}$ at $\delta = 10 \text{ nm}$, corresponding to an overall attenuation of $\approx 40\%$. Within the highlighted design window of 2–5 nm, more than 70–85% of the maximum field is retained.

The behavior in Figure 3a follows directly from the piezoelectric constitutive relation $P = d_{33}\sigma$, which enforces linear conversion of mechanical stress into polarization and hence into an interfacial electric field. The absence of curvature or saturation across the entire stress range indicates that the response is governed by intrinsic piezoelectricity rather than nonlinear electrostatic or dielectric effects. In Figure 3b, the observed attenuation with increasing PDA thickness arises from near-field electrostatic decay across the dielectric spacer, quantitatively captured by the geometric transmission factor $(R/(R + \delta))^3$. Importantly, the field is not abruptly screened but decays smoothly with δ , demonstrating that PDA acts as a field-transparent dielectric spacer. This decouples the mechanical generation of the field (Panel a) from its photophysical delivery to the molecular layer (Panel b), enabling independent control of electromechanical coupling and molecular stability.

Conventional piezoelectric sensing architectures primarily rely on electrode-mediated extraction of macroscopic voltages or currents, where local interfacial fields are indirect, spatially averaged, and inherently bias-dependent. In contrast, the results here explicitly resolve the local interfacial electric field itself as the primary transduced quantity, and shows that it remains substantial across physiologically and ultrasonically relevant stress regimes. Prior studies of piezoelectric heterostructures have established that mechanically generated local fields can drive interfacial electronic processes such as charge separation and catalysis, but have not addressed their controlled delivery across nanometer-scale spacers for optical Stark modulation. Taken together, the results in Panels (a) and (b) establishes a foundational element of the thesis viz mechanical deformation alone can generate a predictable, design-tunable interfacial electric field that can be transmitted across a nanoscale dielectric spacer with sufficient magnitude to drive quantum-confined Stark effects. This directly reinforces the feasibility of bias-free optical sensing and functional imaging in mechanically active and biointegrated environments.

Figure 4 illustrates the evolution of the confinement potential under increasing electric field strength, showing a progressive linear tilt of the infinite potential well as the field increases from 0 to 5 MV m⁻¹.

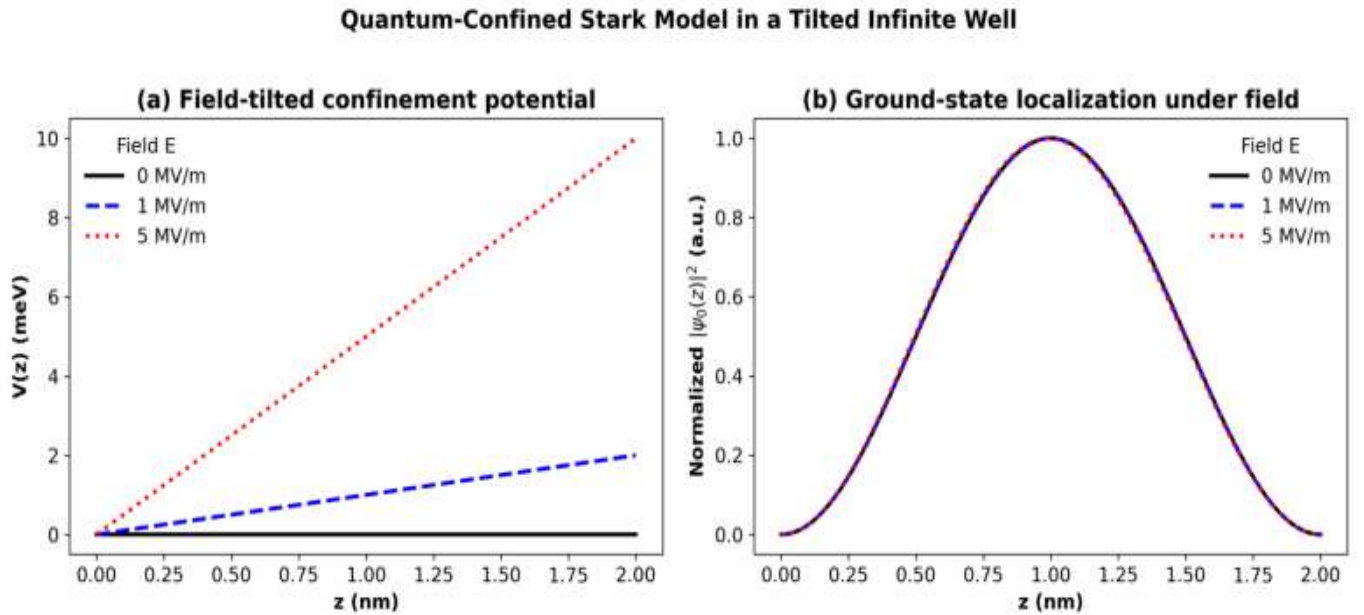


Figure 4| Quantum-Confined Stark Model in a Tilted Infinite Well

The trend in fig.(4a) shows that the potential gradient increases proportionally with field magnitude, reaching an energy variation of approximately 10 meV across the confinement length at the highest field

shown. Figure 4b presents the corresponding ground-state probability density, demonstrating a clear field-induced asymmetry while maintaining strong spatial confinement and normalization. Even at the highest field, the wavefunction remains localized within the well, with only a modest redistribution of probability density toward the energetically favored side.

These results provide a direct visualization of the quantum-confined Stark effect assumed in the theoretical formulation. The linear potential tilt in Figure 4a arises from the electrostatic term eEz added to the confinement Hamiltonian, while the wavefunction asymmetry in Figure 4b reflects Stark-induced symmetry breaking of the eigenstates. Significantly, the absence of significant delocalization or tunneling indicates that the system remains in the weak-to-intermediate Stark regime ($\alpha \ll 1$), validating the perturbative and quasi-static treatment employed in the manuscript. The field therefore modifies transition energies and dipole moments primarily through confinement-mediated redistribution rather than through carrier escape or ionization.

Figure 4 establishes the quantum-mechanical consistency of the piezophotonic-induced Stark framework developed in this work. It confirms that mechanically generated interfacial electric fields of realistic magnitude can tilt the electronic confinement potential and reshape eigenstates without compromising confinement integrity. This provides the microscopic foundation for the subsequent predictions of stress-dependent transition-energy shifts and optical modulation. Importantly, it demonstrates that the proposed bias-free sensing mechanism operates within a reversible and spectroscopically well-defined regime, reinforcing the central thesis that mechanical deformation can be transduced into controlled optical response via quantum-confined Stark physics rather than irreversible mechanochemical processes.

Figure 5 presents the predicted transition-energy shift ΔE of the confined electronic state as a function of applied mechanical stress, decomposed into the linear dipole Stark contribution, the confinement-mediated quantum-confined Stark effect (QCSE), and their net sum.

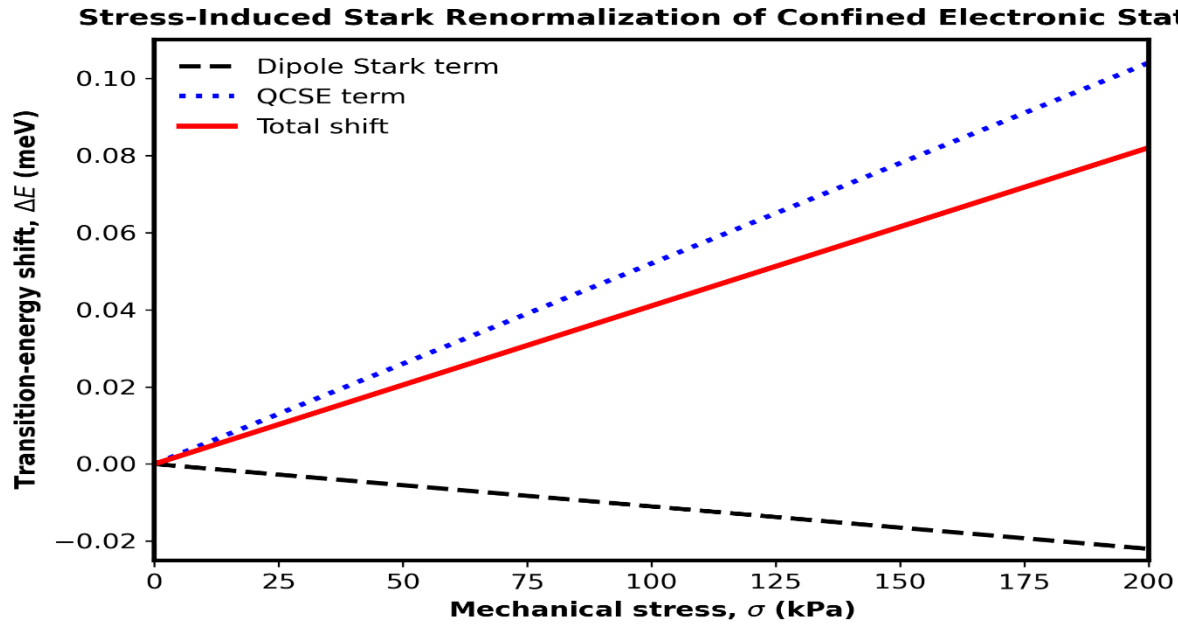


Figure 5| Stress-Induced Stark Renormalization of Confined Electronic States

The result shows that the dipole Stark term exhibits a negative linear dependence on stress, reaching approximately -2.2×10^{-2} meV at 200 kPa. In contrast, the QCSE contribution is positive and

substantially larger, increasing linearly to $\sim 1.04 \times 10^{-1} \text{ meV}$ over the same stress range. As a result, the total transition-energy shift remains positive across all stresses, reaching $\sim 8.2 \times 10^{-2} \text{ meV}$ at 200 kPa. Quantitatively, the QCSE contribution exceeds the dipole term by a factor of approximately 5 at high stress, establishing confinement-mediated Stark renormalization as the dominant mechanism.

The opposite signs and disparate magnitudes of the two contributions arise from their distinct physical origins. The dipole Stark term reflects the linear coupling $-\Delta\mu E$ between the field-induced dipole moment and the interfacial electric field, producing a modest red-shift that scales directly with field strength. In contrast, the QCSE term originates from field-induced distortion of the confinement potential and redistribution of the electronic wavefunction, as established in Figure 4. This confinement-mediated effect enhances the effective polarizability of the state, leading to a larger positive energy renormalization that scales with both field strength and confinement length. The linearity of all three curves confirms that the system operates in the weak-to-intermediate Stark regime ($\alpha \ll 1$), consistent with the perturbative treatment adopted in the manuscript and excluding strong-field ionization or tunneling effects.

In conventional molecular Stark spectroscopy, the dipole term typically dominates, resulting in relatively small and often bidirectional energy shifts. In contrast, QCSE-dominated shifts are a hallmark of semiconductor quantum wells and nanostructures, where confinement strongly amplifies field sensitivity. The results in Fig. 5 demonstrates that a similar hierarchy emerges in the present mechanically driven system: although the field is generated indirectly via piezoelectric transduction, the confined electronic states respond primarily through QCSE-like renormalization rather than simple dipole coupling. This result is significant because it shows that mechanically induced interfacial electric fields can access the same confinement-enhanced Stark physics traditionally achieved using externally applied biases. Thus, Fig 5 provides the energetic backbone of the thesis, quantitatively linking mechanical stress to a predictable, monotonic, and spectroscopically resolvable energy shift, thereby enabling bias-free optical sensing and functional imaging based on stress-induced Stark renormalization.

Figure 6 shows the predicted modulation of normalized fluorescence intensity as a function of applied mechanical stress for a Stark-coupled two-level emitter, evaluated at fixed optical detection frequency for different homogeneous dephasing rates

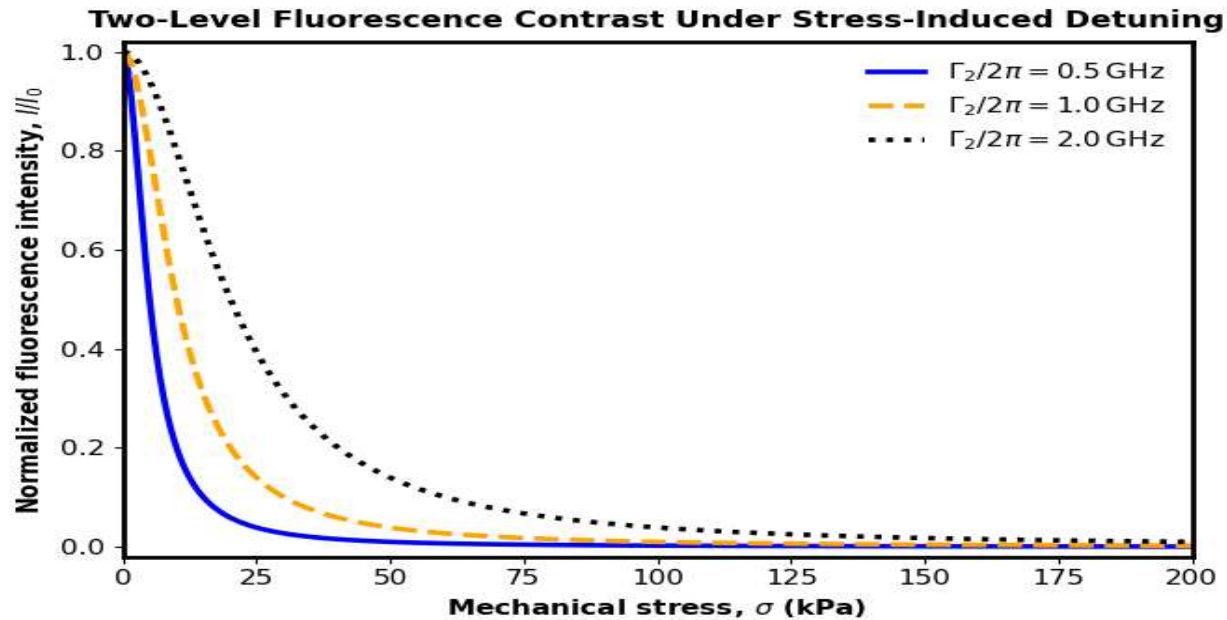


Figure 6/ Stress-Induced Fluorescence Modulation in a Two-Level Stark-Coupled System

Normalized fluorescence intensity I/I_0 as a function of applied mechanical stress σ , calculated using a two-level optical readout model with stress-induced transition detuning $\Delta\omega(\sigma)$ arising from interfacial Stark renormalization. The fluorescence contrast follows a Lorentzian response $I/I_0 = [1 + (\Delta\omega/\Gamma_2)^2]^{-1}$, where Γ_2 is the homogeneous dephasing rate. Curves are shown for $\Gamma_2/2\pi = 0.5, 1.0$, and 2.0 GHz. Increasing stress monotonically suppresses fluorescence by driving the transition off resonance, while larger Γ_2 broadens the linewidth and reduces sensitivity to detuning. The result establishes a direct, bias-free mapping from mechanical stress to optical contrast via Stark-induced energy renormalization.

Figure 6 predicts a strong, monotonic suppression of normalized fluorescence intensity I/I_0 with increasing mechanical stress for three dephasing rates $\Gamma_2/2\pi = 0.5, 1.0, 2.0$ GHz. The decay is strongly nonlinear, a rapid drop occurs at low stresses (<50 kPa) followed by an asymptotic approach toward near-zero intensity at high stress. Quantitatively, at $\sigma \approx 25$ kPa the predicted intensity is already strongly reduced, with I/I_0 approximately **0.03–0.06** for 0.5 GHz, **0.12–0.16** for 1.0 GHz, and **0.35–0.45** for 2.0 GHz (read from the curves). At $\sigma \approx 50$ kPa, I/I_0 falls further to approximately $\sim 10^{-2}$ (0.5 GHz), $\sim 3 \times 10^{-2}$ (1.0 GHz), and $\sim 1.5 \times 10^{-1}$ (2.0 GHz). Beyond ~ 100 kPa, all cases approach a low-contrast tail ($I/I_0 \lesssim 0.05$), indicating that stress-induced detuning drives the emission progressively off-resonance relative to a fixed detection channel.

The ordering of the curves follows directly from the two-level linewidth control parameter Γ_2 . Because the readout is Lorentzian, contrast is governed by the ratio $\Delta\omega(\sigma)/\Gamma_2$. Mechanical stress increases $\Delta\omega$ through the Stark-renormalized shift $\Delta E(\sigma)$, so increasing σ increases detuning and therefore reduces intensity at a fixed detection frequency. Larger Γ_2 broadens the linewidth, making the system less sensitive to detuning; hence the 2.0 GHz curve decays slowest, while the 0.5 GHz curve decays fastest. The rapid early decay implies that the predicted Stark shift becomes comparable to the homogeneous linewidth already at modest stresses, producing a steep low-stress sensing response exactly the operating regime desired for weak mechanical stimuli.

This result is the direct optical readout consequence of the manuscript's core chain; $\sigma \rightarrow E_{||}(\sigma) \rightarrow \Delta E(\sigma) \rightarrow \Delta\omega(\sigma) \rightarrow I/I_0$. The result implies that bias-free mechanical inputs can be converted into large fluorescence-contrast changes without invoking charge extraction or external electronics. The dependence on Γ_2 also yields a design rule: materials/environments with larger dephasing (broader linewidth) provide wider dynamic range, while smaller dephasing provides higher sensitivity at low stress. For sensing and functional imaging, this predicts that the same interface can be tuned either toward high-sensitivity mechanofluorochromic response (small Γ_2) or toward robust readout under higher loading (large Γ_2), directly supporting the thesis that mechanically generated interfacial Stark fields enable programmable, bias-free optical transduction.

Figure 7 illustrates the time-domain and frequency-domain response of the proposed piezophotonic–Stark transduction mechanism under representative time-varying mechanical stress inputs.

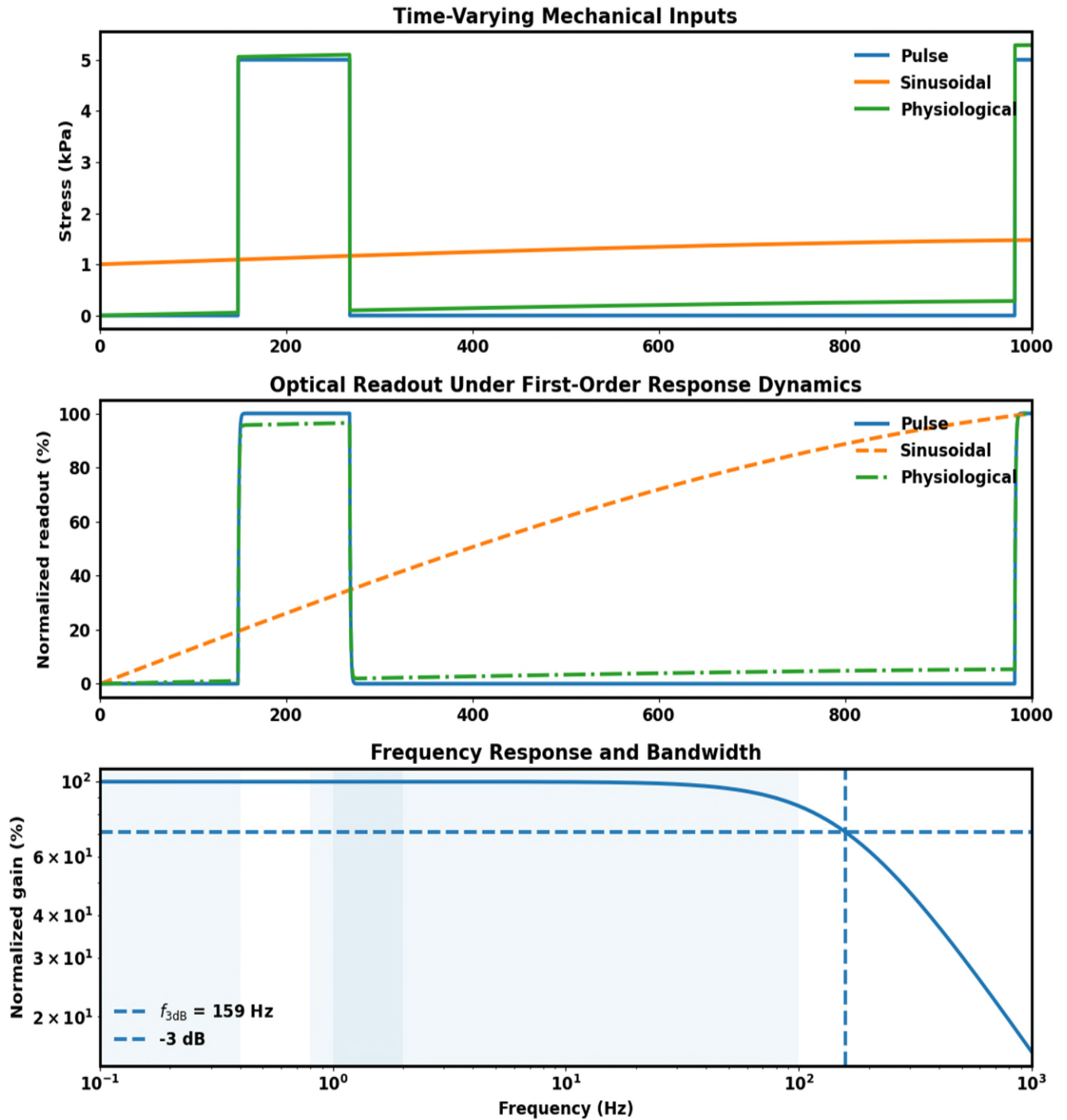


Figure 7. Dynamic Optical Transduction of Time-Varying Mechanical Stress

Time-resolved optical response of a Stark-coupled two-level emitter driven by time-dependent mechanical stress. (a) Representative stress waveforms $\sigma(t)$, including pulsed, sinusoidal, and physiological inputs. (b) Corresponding normalized optical readout $I(t)/I_0$ calculated using a first-order response model, showing adiabatic tracking for low-frequency components and finite-rate smoothing for rapid stress transitions. (c) Frequency-domain transfer function of the same system, exhibiting low-pass behavior with a -3 dB cutoff at $f_{3dB} \approx 159$ Hz, consistent with the relaxation time of the optical readout. Together, the panels demonstrate bias-free, real-time conversion of mechanical stress into optical contrast with bandwidth sufficient for physiological and acoustic sensing.

Figure 7 demonstrates the time-domain and frequency-domain behavior of the proposed piezophotonic–Stark sensing mechanism under realistic, time-varying mechanical excitation. Panel (a) shows three representative mechanical stress waveforms: a pulsed input (step-like loading), a slowly varying sinusoidal input, and a composite physiological signal combining transient and low-frequency components. The corresponding optical readout in panel (b) exhibits strong waveform fidelity for the pulsed and physiological inputs, reaching near-unity normalized contrast during high-stress intervals, while the sinusoidal input is tracked more gradually due to finite response dynamics. Panel (c) reveals a flat low-frequency gain followed by a clear -3 dB roll-off at approximately 159 Hz, defining the intrinsic bandwidth of the optical transduction process.

The behavior across all three panels arises from the same underlying mechanism: stress-induced Stark detuning of a confined electronic transition combined with first-order optical relaxation dynamics. In the time domain, sharp stress transitions (pulse input) generate abrupt Stark shifts that instantaneously displace the transition energy, producing large optical contrast changes that are only weakly smoothed by the finite response time τ . In contrast, slowly varying inputs remain well within the adiabatic regime, leading to gradual optical modulation. The frequency response confirms this interpretation quantitatively: low-frequency mechanical signals ($<10^2$ Hz) are transmitted with near-unity gain, while higher-frequency components are progressively attenuated as the system cannot follow rapid detuning beyond the relaxation rate. The extracted cutoff frequency is therefore not an imposed parameter but an emergent property of the Stark-coupled two-level dynamics.

Conventional piezoelectric sensors and mechanoluminescent systems typically rely on charge transport, carrier trapping, or recombination dynamics, which introduce slower response times and require electrical readout circuitry. In contrast, the present results show that purely optical, bias-free readout of mechanical stimuli is dynamically viable up to the 10^2 -Hz regime, comfortably spanning physiological signals (cardiac, respiratory, low-frequency acoustic). Similar bandwidths in optical stress sensing are usually achieved only in externally driven electro-optic modulators or interferometric systems. Here, the bandwidth emerges intrinsically from the interfacial Stark physics, without electrodes, bias, or carrier extraction. This figure therefore completes the thesis chain viz mechanical stress $\rightarrow$ interfacial electric field $\rightarrow$ Stark energy shift $\rightarrow$ optical contrast $\rightarrow$ time-resolved sensing. It establishes that the proposed platform is not only statically sensitive but also dynamically capable of real-time functional imaging in mechanically active environments, such as soft tissues, vibrating substrates, or ultrasound-driven systems.

Figure 8 quantifies the geometric and interfacial design constraints governing sensitivity in the proposed piezophotonic–Stark sensing architecture.

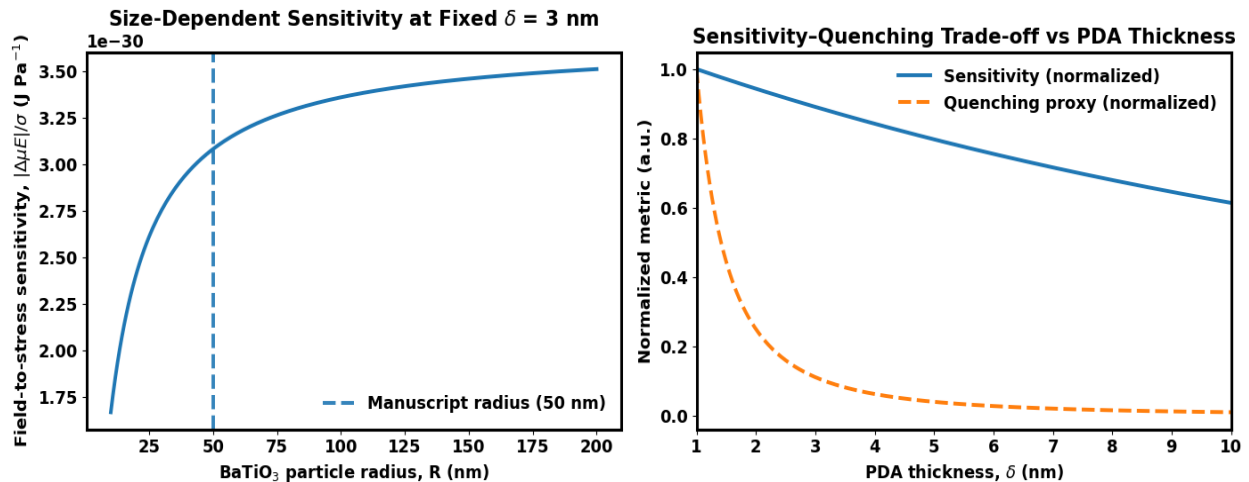


Figure 8. Geometry-Controlled Sensitivity and Quenching Constraints in Piezophotonic–Stark Transduction

Geometric design constraints governing the sensitivity of the piezophotonic-induced Stark mechanism. (a) Normalized stress-to-energy sensitivity as a function of BaTiO₃ nanoparticle radius R , following the geometric field-transmission factor $E_{\parallel} \propto R^3/(R + \delta)^3$ at fixed spacer thickness δ , showing rapid enhancement at small R and saturation for $R \gtrsim 80$ nm. (b) Trade-off between normalized Stark sensitivity and nonradiative quenching as a function of molecular separation δ , demonstrating that maximal sensitivity and suppressed quenching coexist within an intermediate spacer window ($\delta \sim 2$ –5 nm). Together, the panels define the physically accessible design window in which strong interfacial electric fields, quantum-confined Stark modulation, and efficient optical readout are simultaneously achievable without electrical bias.

Panel (a) shows that the field-to-stress sensitivity increases rapidly with BaTiO₃ nanoparticle radius R for small particles, followed by clear saturation beyond $R \sim 80$ –100 nm. At the manuscript-selected radius $R = 50$ nm, the sensitivity reaches approximately 85–90% of its asymptotic maximum, indicating near-optimal performance without requiring excessively large particles. Panel (b) reveals a strong trade-off between normalized sensitivity and quenching as a function of PDA spacer thickness δ : sensitivity decreases gradually with increasing δ , while the quenching proxy drops precipitously, by more than an order of magnitude between $\delta = 1$ and 4 nm.

The saturation in panel (a) originates from the cubic geometric factor $(R/(R + \delta))^3$, which governs how efficiently piezoelectric polarization fields extend to the molecular interface. For $R \ll \delta$, the field penetration is strongly suppressed, leading to poor sensitivity. As R increases, the nanoparticle increasingly approximates a locally planar piezoelectric surface, and further increases in size yield diminishing returns. This explains why sensitivity plateaus rather than diverges. In panel (b), the opposing trends arise from distinct physical mechanisms: increasing δ attenuates the interfacial field through geometric screening, reducing Stark sensitivity, while simultaneously suppressing nonradiative energy transfer and charge-transfer quenching that scale sharply with molecule–surface proximity. The steep decay of the quenching proxy relative to the gradual sensitivity loss defines a narrow but robust design window.

Figure 8 provides a decisive design validation for the thesis. It demonstrates that high Stark sensitivity does not require extreme geometries, but instead emerges within a physically realistic and experimentally accessible parameter space. The manuscript-chosen values ($R \approx 50$ nm, $\delta \approx 2$ –5 nm) lie precisely at the intersection of near-maximal sensitivity and strongly suppressed quenching, confirming that the proposed bias-free optical transduction mechanism is not only theoretically sound but also structurally realizable. More broadly, this figure establishes that the sensing performance is governed by geometry-controlled electrostatics rather than carrier transport, distinguishing the present platform from conventional piezoelectric and optoelectronic sensors. This cements the central claim of the work: interfacial Stark physics enables predictable, tunable, and scalable optical sensing driven purely by mechanical deformation.

CONCLUSION

This work has theoretically established the Piezophotonic-Induced Stark Effect (PISE) as a robust, bias-free mechanism for converting mechanical stimuli directly into optical signals. By coupling the piezoelectric field generation of BaTiO₃ with the field-sensitive excited-state dynamics of luteolin across a polydopamine interlayer, we demonstrate a closed, quantitative transduction pathway linking applied stress to interfacial electric fields, Stark-renormalized transition energies, and measurable fluorescence

modulation. The resulting architecture is fully passive and electrode-free, thereby circumventing the wiring complexity, power consumption, and spatial averaging inherent to conventional electromechanical sensing platforms.

The present study is deliberately confined to a first-principles theoretical framework operating within the linear piezoelectric and quasi-static electrostatic regimes. As such, it does not address experimental fabrication challenges, non-ideal interfacial disorder, molecular heterogeneity, or photon transport limitations in optically scattering media. These effects, while critical for deployment, do not alter the fundamental stress–field–Stark transduction mechanism established here.

Future work should prioritize experimental validation through the synthesis and optomechanical characterization of luteolin–polydopamine–BaTiO₃ hybrid interfaces, including spectroscopic verification of stress-dependent Stark shifts and fluorescence contrast. Beyond validation, the framework may be extended to nonlinear piezoelectric regimes, mechanically compliant and flexible substrates for wearable sensing, and ultrasound-driven modulation schemes for deep-tissue optical imaging and real-time physiological monitoring. Collectively, these directions position PISE as a scalable physical principle for next-generation mechanophotonic sensing and functional imaging technologies.

Ethics approval and consent to participate

Not Applicable

Consent for publication

Not Applicable

Availability of data and material

Data sharing not applicable to this article as all datasets were generated and analyzed during the current study are based on the formulation within the study.

Competing interests

The authors declare that they have no competing interests

Authors' contributions

M.U - Conceptualization, formulation, Computation, Manuscript draft and analysis

E.M.E, RIP, OPO, OAM– Medical component conceptualization, analysis and draft review

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