Tunable omnidirectional strong light-matter interactions mediated by graphene surface plasmons

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In this theoretical work, we report on voltage-controllable hybridization of electromagnetic modes arising from strong interaction between graphene surface plasmons and molecular vibrations. The interaction strength depends strongly on the volume density of molecular dipoles, the molecular relaxation time, and the molecular layer thickness. Graphene offers much tighter plasmonic field confinement and longer carrier relaxation time compared to noble metals, leading to Rabi splitting and hybridized polaritonic modes at three-orders-of-magnitude lower molecular densities. Electrostatically tunable carrier density in graphene allows for dynamic control over the interaction strength. In addition, the flat dispersion band above the light line arising from the deep confinement of the polaritonic modes gives rise to the omnidirectional excitation. Our approach is promising for practical implementations in infrared sensing and detection.

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Strong light-matter interactions are of interest for both fundamental studies and nonubiquitous applications. Such interactions lead to formation of new hybrid states with mixed properties of their uncoupled constituent states as well as unusual properties possessed by neither.¹⁻¹¹ Within the context of microcavities, vacuum quantum Rabi splitting arising as a result of strong coupling between a single emitter and a high-quality-factor (Q-factor) resonator has been studied extensively.^{3–15} New possibilities for strong lightmatter interactions have been enabled by the emergence of the field of nanoplasmonics.^{16–24} Both localized and propagating surface plasmon modes can be utilized to achieve strong localization and enhancement of electromagnetic fields.²⁵ These features of metal surface plasmons have been widely explored for surface enhanced spectroscopy and proximity sensing.^{26–28} More recently, new polariton modes with unique dispersion characteristics due to strong polaritonic modal coupling between molecular excitons and plasmon modes, mediated by strong field confinement in metal nanostructures, have been demonstrated.^{29,30}

Typically, the Purcell factor that is proportional to the ratio of the Q factor of the photonic or plasmonic resonance to the effective mode volume gives a good measure of the interaction strength.^{31,32} In plasmon-mediated strong polaritonic coupling, very small mode confinement compensates for low quality factors ($Q \sim 10$) inherent to plasmonic resonances. Large Purcell factors to achieve spontaneous rate enhancement in plasmonic structures have been reported.³³ However, for Rabi splitting, we note that for plasmonic resonators the interesting case is the coupling between an ensemble of oscillators and the plasmonic resonant mode, analogous to multiatom Rabi splitting.⁹ This is opposed to the case of "strong coupling," which is strictly reserved for the purely quantum mechanical interaction between a single emitter and an emitted photon leading to new energy states due to this perturbation. Therefore, we make a distinction here and refer to this plasmon-mediated coupling as "strong interaction" to distinguish this from "strong coupling."

Recently, graphene, a two-dimensional (2D) semimetal consisting of a honeycomb lattice of carbon atoms, emerged as a new plasmonic material for infrared and terahertz regions.^{34–39} Compared to metals, plasmons of doped graphene are much better confined ($\sim 10^6$ smaller than diffraction limit), offering stronger light-matter interactions.³⁵ On the other hand, as a 2D electron gas system, the charge carriers near the Dirac point of the electronic band structure are nearly massless and can propagate micrometers without scattering even at room temperature⁴⁰ (typical γ , the damping rate, is $10^{11}-10^{13}$ s⁻¹), which leads to a longer plasmon propagation length. Additionally, the plasmon modes of graphene can be dynamically tuned via electrostatic doping, which is particularly important for practical nanoplasmonic devices.⁴¹

Here, we study the interaction between infrared vibrational modes of molecules and graphene surface plasmons (GSPs). We report hybrid states arising due to the strong interaction between molecular vibrations and GSPs excited via a subwavelength dielectric grating such that the second-order Bragg condition is satisfied for the GSP mode for normal incidence. The interaction strength can be dynamically controlled by the electrostatically tunable carrier density in graphene. We further show that the interaction strongly depends on the density of molecular dipoles, the molecular damping, and the molecular layer thickness. An additional collective mode is supported for the high-density and low-damping molecular system along with the anticrossing hybridization states for the low molecular density or high damping. Utilizing the flat photon dispersion of the hybrid modes above the light line and the tunable Fermi energy of graphene, we further propose a tunable omnidirectional sensing platform.

The common approaches to generate GSPs include patterning the graphene,^{38,39,42} the substrate,^{43–46} or using nanoscale metal tips.^{47,48} In order to preserve the excellent electrical properties and to facilitate the tuning of doping level of graphene, we favor the patterned dielectric substrate to excite GSPs. We analyze a graphene-covered one-dimensional dielectric grating with a period of $\Lambda = 300$ nm, thickness t = 300 nm, and width d = 150 nm (i.e., the filling factor f is 0.5), as illustrated in Fig. 1(a). The dielectric constant, ε , of the material is assumed to be a constant 2.3 (e.g., KBr). The temperature-dependent optical conductivity of graphene is modeled using the result from the Kubo formalism within the local random-phase approximation.^{49,50} We assume a Fermi



FIG. 1. (Color online) (a) Grating structure for GSP excitation and the free-standing molecular layer with periodicity $\Lambda = 300$ nm, width d = 150 nm, and thickness of the dielectric strip ($\varepsilon = 2.3$) t = 300 nm. The incident angle is θ . (b) Absorbance spectra of GSPs excited via a subwavelength dielectric grating under normal incidence (black circles) and a 1-nm-thick free-standing molecular layer with low density ($N_m = 7.2 \times 10^{21} \text{ m}^{-3}$) (red rectangles) and high density ($N_m = 3.19 \times 10^{23} \text{ m}^{-3}$) (orange triangles), respectively. The parameters for graphene and the molecules are $E_F = 0.4$ eV, $\tau = 0.4$ ps, $\varepsilon_{\infty} = 2, \omega_m = 130.4 \text{ meV}$ (i.e., 9.48 μ m), and $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$. In the inset, the intersection point of the GSP dispersion curve (solid line) and the first-order reciprocal vector ($2\pi/\Lambda$) provided by the grating (dashed line) shows good agreement with the numerical peak.

level of $E_F = 0.4$ eV and an intrinsic relaxation time of $\tau = 0.4$ ps corresponding to a direct current (DC) mobility of $\mu = 10000$ cm² V⁻¹ s⁻¹⁵¹ at room temperature (T = 300 K). In our electromagnetic calculations, we assume normally incident plane waves with an electric field polarized along the *x* direction (i.e., *p*-polarization).

Due to the conservation of momentum, the condition for GSP excitation can be analytically expressed as $|\mathbf{q}| = |\mathbf{k}_x + \mathbf{G}_x|$, where \mathbf{q} is the wave vector of GSP, \mathbf{k}_x is the in-plane wave vector of the incident light with the wave vector $|\mathbf{k}| = \omega/c, \omega$ is the frequency of incident light, *c* is the speed of light in a vacuum, and \mathbf{G}_x is the reciprocal lattice vector ($\mathbf{G}_x = 2\pi \hat{\mathbf{x}}/\Lambda$, where $\hat{\mathbf{x}}$ is the unit vector in the *x* direction). The excited GSP wave propagates along the surface, which follows the Bloch theorem $\Psi(\mathbf{r} + \Lambda) = e^{i\mathbf{k}\cdot\Lambda}\Psi(\mathbf{r})$, where \mathbf{r} is the position vector and Ψ is the field. By using $q = |\mathbf{q}| = i\varepsilon_0\omega(\varepsilon_1 + \varepsilon_2)/\sigma$ from the electrostatic limit of the GSP dispersion relation,^{35,36} the wavelength in free space λ_{GSP} which can excite a GSP is, therefore, determined [the inset of Fig. 1(b)] according to the formula

$$\lambda_{\rm GSP} = \frac{i c \varepsilon_0 (\varepsilon_1 + \varepsilon_2) \Lambda}{\sigma}, \quad (k_x = 0), \tag{1}$$

where ε_0 is the vacuum permittivity, σ is the conductivity of graphene, and ε_1 and ε_2 are the effective permittivity of the dielectric media on either side of the graphene. For instance, the effective permittivity of the KBr grating is 1.65 by applying

the formula $\varepsilon_2 = f \varepsilon_1 + (1 - f)$. The analytical results show that the first GSP resonance occurs at the energy E =133.0 meV (9.30 μ m), in good agreement with the numerical results [Fig. 1(b)], which indicates an absorption peak located at 131.2 meV (9.43 μ m). All numerical results in the paper are calculated using a two-dimensional implementation of the scattering matrix method.^{43,52} The central idea of the scattering matrix method is to relate the electric and magnetic fields in different regions by a 2 × 2 matrix. The matrix can be obtained by solving the Maxwell's equations and applying proper boundary conditions. Within the framework of this approach, it is possible to calculate the reflectance, transmittance, and absorption.

Having verified the GSP excitation condition, we consider the electromagnetic coupling between GSPs and molecular vibrational modes. To this end, we assume a molecular layer covering the graphene surface. To model the absorption of an ensemble of molecules, the Drude-Lorentz type dispersion is applied to describe the macroscopic dielectric constant of the molecular layer

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{e^2 N_m / (\varepsilon_0 m_e)}{\omega_m^2 - \omega^2 - i \gamma_m \omega},$$
(2)

where ε_{∞} is the dielectric constant of the system at high frequencies (e.g., $\varepsilon_{\infty} = 2$), *e* is the electron charge, m_e is the electron rest mass, N_m is the volume density of molecular dipoles, ω_m is the molecular resonance frequency (e.g., $\omega_m =$ 130.4 meV in order to match the GSP resonance), and γ_m is the molecular damping (e.g., $\gamma_m = 1 \times 10^{12}$ rad s⁻¹ in the following simulations unless otherwise specified). The extinction spectra of such a 1-nm-thick free-standing film (i.e., not coupled to graphene grating structure) shows only 0.3% absorption with N_m on the order of 10^{21} m⁻³ and ~12% for 10^{23} m⁻³ [Fig. 1(b)], respectively.

When a low density of molecules (e.g., $N_m = 7.2 \times$ 10²¹ m⁻³) are adsorbed onto graphene, the direct absorption by the molecules is low. The interaction between the molecules and the strong GSP near-field can enhance the molecular absorption. Therefore, the energy exchange between GSPs and the molecules is large, provided that the GSP modes and the molecular vibrations are spectrally matched. This leads to a splitting of the infrared absorption spectra at the position of the molecular vibrational resonance, which is very similar to Rabi splitting for the case of many atoms in an optical cavity.53 Similarly to Fano resonances,54,55 this can be understood by solving the problem of two independently driven coupled oscillators within the framework of classical mechanics.^{53,56} Furthermore, we observe that the interaction strength can be modified by changing the E_F of graphene (e.g., by electrostatically gating). Figure 2(a) illustrates the variation of the coupled hybrid modes with different E_F . Similar mode splitting is observed in all cases, and they progressively red-shift with decreasing E_F as a result of red-shifting GSP resonance. We can understand this phenomenon by plotting the relationship between the peak positions and the E_F . Interestingly, an energy gap between the upper and lower anticrossing hybridized polaritons $[E_u \text{ and } E_l, \text{ solid circles in}]$ Fig. 2(b)] emerges. For $E_F = 0.4$ eV, the value of the energy gap is $2\Delta = 2.13$ meV. By solving the eigenvalue problem of



FIG. 2. (Color online) The absorption spectra [(a), (c), and (e)] and the hybridized polaritons [(b), (d), and (f)] under different molecular densities and damping. The 1-nm-thick molecular layer is situated on the graphene coupled to the subwavelength dielectric grating. [(a) and (b)] $N_m = 7.2 \times 10^{21} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(c) and (d)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$, $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$; [(e) and (f)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$; [(c) and (d)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$; [(c) and (d)] $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$; [(c) and (d

the interaction Hamiltonian

$$\hat{H}\Psi = E_{u,l}\Psi,\tag{3}$$

where $\hat{H} = \begin{pmatrix} E_m & \Delta \\ \Delta & E_g \end{pmatrix}$, Ψ is the eigenvector, E_g is the GSP resonance excitation energy without molecules, and E_m is the molecular resonance energy (130.4 meV) [red dashed lines in Figs. 2(b), 2(d), and 2(f)], the energies of the newly formed hybrid polaritons can be analytically calculated as^{57,58}

$$E_{u,l}(E_F) = \frac{[E_g(E_F) + E_m]}{2} \pm \sqrt{\Delta^2 + \frac{[E_g(E_F) - E_m]^2}{4}}.$$
(4)

The obtained results are plotted in Figs. 2(b), 2(d), and 2(f) (open circles). From Fig. 2, it can be seen that the analytical solutions are in good agreement with the numerical ones. In addition, the inset in Fig. 2(b) shows the linear dependence of the splitting on $\sqrt{N_m}$ at low molecular density under $E_F = 0.4$ eV, as expected for multiatom Rabi splitting.⁹

When the density of molecules increases to a higher level (e.g., $N_m = 3.19 \times 10^{23} \text{ m}^{-3}$), the direct molecular absorption becomes significant. We again calculate the absorption spectra as a function of different Fermi energies of graphene [Fig. 2(c)]. It is observed that an additional peak emerges at the molecular transition energy as a consequence of collective molecular interactions,²⁴ although the other two peaks show the similar red-shifting with decreasing E_F . From Fig. 2(d) (solid circles), the mode shows much larger energy splitting

compared to the low-density case, with a separation value of ~ 11.21 meV at $E_F = 0.4$ eV as a result of stronger near-field coupling. More characteristically, the peak between the two GSP-molecule hybridized states manifests that it is largely independent of E_F , indicating that it is of a molecular origin.

With the high density of the molecular dipoles ($N_m = 3.19 \times 10^{23} \text{ m}^{-3}$), Fig. 2(e) shows that the molecular collective mode is negligible as the molecular damping is assumed to be a higher value of $\gamma_m = 1 \times 10^{13} \text{ rad s}^{-1}$, manifesting an anticrossing polariton behavior similar to the results in the low-density and low-damping molecule system [solid circles, Fig. 2(f)]. In addition, the splitting peaks become broader as well as weaker, and the energy gap between the hybridized modes decrease to 10.435 meV at $E_F = 0.4 \text{ eV}$. For polariton modes, larger molecular damping weakens the interaction between the GSPs and the molecular vibrational modes, exhibiting, due to higher damping, broader hybridized peaks and shrinkage of the energy gap. The analytical results show good agreement with the numerical calculations.

Not only the density and damping of molecules influence the interaction strength; the thicknesses of molecular layer also contribute to the mode hybridization. The molecular dipoles can "feel" the near-field of the excited GSPs and exchange energy with the plasmonic field effectively within the attenuation length of the GSPs which is $1/\sqrt{q^2 - |\mathbf{k}|^2}$ (open circles in Fig. 3). At the GSP resonance (i.e., 130.4 meV), the attenuation length reads ~50 nm (dashed line in Fig. 3). Again, with high density of molecules $N_m = 3.19 \times 10^{23}$ m⁻³



FIG. 3. (Color online) The dependence of the absorption spectra on the molecular layer thickness at $E_F = 0.4$ eV. The density and damping of the molecules are 3.19×10^{23} m⁻³ and 1×10^{13} rad s⁻¹, respectively. The open circles show the GSP attenuation lengths for different energies and the dashed line denotes the value for E = 130.4 meV.

and high damping $\gamma_m = 1 \times 10^{13}$ rad s⁻¹, we calculate the absorption spectra dependence on the molecular layer thickness (Fig. 3). As expected, the energy splitting grows rapidly as the molecular layer thickness increases within the attenuation length but insignificantly beyond that. Besides, the interaction between the GSPs and the molecular dipoles near the graphene is full, whereas it is insufficient away from the surface,²⁴ resulting in an asymmetric energy splitting with the increasing molecular thickness. Another attribute revealed in Fig. 3 is that, interestingly, the molecular collective mode becomes prominent, as the layer thickness increases, as a result of larger number of molecular dipoles involved.

The fact that the character of the spectral response depends on the molecular density and the molecular damping, together with the dynamically controllable E_F of graphene, implies the potential for ultrasensitive molecular detection and sensing. For this purpose, we define the intensity modulation depth δI and energy splitting δE as

$$\delta I = \frac{I - I_m}{I}, \quad \delta E = \frac{E_u - E_l}{\Delta E},\tag{5}$$

where *I* is the intensity of the reference spectra, I_m is the spectral intensity of the hybrid graphene-molecule system, and ΔE is the full width at half maximum (FWHM) of the reference spectra in units of energy. We note that the reference spectra is taken to be the case where graphene is covered with a 1-nm-thick layer with a purely real dielectric constant equal to ε_{∞} in order to cancel the detuning of the plasmonic response from the local refractive index change due to the imposed molecular layer. For a given 1-nm-thick graphene layer ($E_F = 0.4$ eV and $\tau = 0.4$ ps) and a fixed molecular absorption resonance frequency $\omega_m = 130.4$ meV, δI and δE are plotted as functions of N_m and τ_m , where τ_m is the molecular relaxation time ($\tau_m = 1/\gamma_m$) [Figs. 4(a) and 4(b)].

molecular relaxation time ($\tau_m = 1/\gamma_m$) [Figs. 4(a) and 4(b)]. For $\tau_m = 2\pi$ ps (i.e., $\gamma_m = 1 \times 10^{12}$ rad s⁻¹), the dependence of δI on N_m [solid black circles in Fig. 4(a)] shows that the maximum intensity variation of ~80% occurs as N_m reaches the value of 3.9×10^{22} m⁻³. Subsequently, the



FIG. 4. (Color online) Dependence of δI (solid black) and δE (open red) on molecular densities [with a fixed relaxation time $\tau_m = 2\pi$ ps in (a)] and molecular relaxation times [with a fixed molecular density $N_m = 7.98 \times 10^{22}$ m⁻³ in (b)] in graphene.

intensity modulation decreases due to the emergence of the collective modes at high molecular density. We note that the minimum threshold to identify mode intensity change and energy splitting for N_m is as low as $\sim 10^{20}$ m⁻³, which is \sim 3 orders of magnitude lower than the reported value for its metal counterpart.²⁴ The dependence of δE on N_m is rather a monotonically increasing function [open red circles in Fig. 4(a)]. A higher density of molecules gives rise to larger variations in energy splitting up to $4 \times \Delta E$ when N_m is on the order of 10^{23} m⁻³. Similarly, assuming $N_m = 7.98 \times$ 10^{22} m⁻³, after a rapid increase when τ_m has small values, δI [solid black circles in Fig. 4(b)] reaches its maximum value of \sim 80% and subsequently decreases, following the dependence of δI on N_m . The results can be understood since a longer relaxation time leads to sufficient interaction time between the molecular dipoles and GSPs and thus stronger interaction strength to mediate the collective modes. In this aspect, it is likely that the increasing of τ_m has the same role as higher N_m . On the other hand, the effect of τ_m on δE obviously differs from that of N_m [red open circles in Fig. 4(b)]. After a rapid increase, δE remains constant, indicating that the larger GSP damping limits the splitting for larger τ_m .

Following the aforementioned studies, we now propose a tunable omnidirectional ultrasensitive platform for strong light-matter interaction, as depicted in Fig. 5(a). In the proposed device, the optical features are enhanced by coupling the active layer (graphene and molecules) to a Febry-Pérot resonant cavity.⁵⁹ In order to tune E_F of the graphene, a thin layer of opaque metal (e.g., Ag) at the target frequencies is deposited under the substrate as the capacitive back gate, together with top source and drain electrodes. Note that this has the added benefit of suppressing optical transmission without influencing the GSPs excitation, thereby greatly enhancing



FIG. 5. (Color online) (a) The proposed structure for an omnidirectional molecular sensor. The E_F can be tuned by the applied gate voltage V_0 . [(b) and (c)] Both the simulated band structures and the analytical results (dashed lines), calculated at low and high molecular densities at $E_F = 0.4$ eV, show the flat polariton bands above the light lines (black solid lines). By illuminating the structure at different angles, the corresponding reflection spectra are shown in (d) and (e), respectively. The results reveal the strong interaction occurs omnidirectionally and the peaks remain almost stationary. The parameters used in the simulations are: $N_m = 7.2 \times 10^{21}$ m⁻³ for (b) and (d) and $N_m = 3.19 \times 10^{23}$ m⁻³ for (c) and (e), while $\gamma_m =$ 1×10^{12} rad s⁻¹ and the substrate thickness is 1.38 μ m in both cases.

the observable reflection. Subsequently, the molecules can be identified by measuring the reflection spectra of the device. Inherent to the deep subwavelength confinement of the GSPs, the polaritons manifest flat bands [Figs. 5(b) and 5(c)] above the light line (black solid lines in the figure) at different molecular concentration and damping. The analytical polariton

band structures obtained via the transfer matrix derivation [dashed lines in Figs. 5(b) and 5(c)] exhibit similar features with that of the numerical results.^{46,60} From the band diagrams, we emphasize that the hybridized modes can be excited omnidirectionally. That is, the observed reflection spectra are maintained as well with negligible shifting by the omnidirectional excitation [(Figs. 5(d) and 5(e)], which is particularly useful in practical implementations. Unlike traditional sensors, the optical features of the proposed application are easy to be tuned uniquely by doping graphene via the applied gate voltage V_0 . The dynamic tuning even enables the *in situ* detection of mixed molecules with different "fingerprint" infrared absorption peaks. As such, the proposed graphene-enabled sensor has great potential for molecule identification and *in situ* process identification such as chemical reaction monitoring.

In conclusion, graphene is an ultrasensitive platform for strong light-matter interactions. In the nanoscale-tip plasmonexcitation and graphene strip systems, strong interaction is revealed between GSPs and SiO₂ surface phonons⁴⁷ or graphene intrinsic phonons.⁴² Here we reveal the nature of the energy exchange between the molecular vibrations induced by infrared absorption and the strong near-field of excited GSPs. The results show that the interaction occurs coherently, leading to strong interaction, even for a 1-nm-thick layer. At low molecular density or high damping, the GSP peak splits at the molecular resonance energy, resulting in two hybridized polaritonic modes. At high molecular density and low damping, an additional collective mode at the molecular resonance emerges, which is predominantly due to the direct molecular absorption. From the dependence of δI and δE on molecular parameters, we find that the strong interaction depends on the density and relaxation times of molecular dipoles, which implies the ability to identify and distinguish between various molecular types and densities. Further investigations show that the energy splitting also depends on the molecular layer thickness, as a result of effective interaction between GSPs and molecular dipoles within the GSP attenuation length. Such strong interactions can also occur in analogous metal structures; however, the lower carrier scattering time and degree of plasmon confinement results in much inferior sensitivities to graphene sensors. By utilizing flat dispersion of the hybrid modes and the tunable graphene doping levels, we propose a tunable omnidirectional sensor which is potentially applicable in a wide variety of fields, ranging from in situ molecule recognition, chemical or biomolecular sensing, photochemistry monitoring, and even nonlinear optics.⁶¹

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