Tailoring light-matter interactions via plasmonic nanoantennas (PNAs) has emerged as a breakthrough technology for spectroscopic applications. The detuning between molecular vibrations and plasmonic resonances, as a fundamental and inevitable optical phenomenon in light-matter interactions, reduces the interaction efficiency, resulting in a weak molecule sensing signal at the strong detuning state. Here, it is demonstrated that the low interaction efficiency from detuning can be tackled by overcoupled PNAs (OC-PNAs) with a high ratio of the radiative to intrinsic loss rates, which can be used for ultrasensitive spectroscopy at strong plasmonic-molecular detuning. In OC-PNAs, the ultrasensitive molecule signals are achieved within a wavelength detuning range of $248 \text{ cm}^{-1}$, which is $173 \text{ cm}^{-1}$ wider than previous works. Meanwhile, the OC-PNAs are immune to the distortion of molecular signals and maintain a lineshape consistent with the molecular signature fingerprint. This strategy allows a single device to enhance and capture the full and complex fingerprint vibrations in the mid-infrared range. In the proof-of-concept demonstration, 13 kinds of molecules with some vibration fingerprints strongly detuning by the OC-PNAs are identified with 100% accuracy with the assistance of machine-learning algorithms. This work gains new insights into detuning-state nanophotonics for potential applications including spectroscopy and sensors.

1. Introduction

Plasmonic nanoantennas (PNAs) are artificial subwavelength structures with highly confined electromagnetic hotspots and the ability to manipulate light at the subwavelength scale, thus offering unique opportunities to enhance light-matter interactions.\(^{[1]}\) Huge applications have been developed due to this feature, such as enhanced spectroscopy,\(^{[2]}\) nonlinear photonics,\(^{[3]}\) plasmonic catalysis,\(^{[4]}\) quantum photonics,\(^{[5]}\) and nanolasers.\(^{[6]}\) In particular, the emergence of PNAs solves the limitation of the low sensitivity of infrared spectroscopy when detecting a small number of molecules or ultra-thin film systems\(^{[7-10]}\) and injects new vitality into traditional infrared spectroscopy techniques. Consequently, PNAs have been widely used in sensing fields involving molecular vibrations, including dynamic reaction monitoring,\(^{[11-13]}\) hyperspectral infrared imaging,\(^{[14-16]}\) and biochemical molecular detection.\(^{[17-19]}\) However, the bandwidth of PNAs with enhancement effects is limited because the spectral resonances ($\omega_0$) produced by PNAs are sharp and high-Q (quality factor). When the molecular fingerprint vibration frequency ($\omega_m$) is off the plasmon resonance (spectral detuning), the light-matter interaction decays sharply. Interaction decay at spectral detuning limits the practical applications of PNAs such as the identification of trace molecules for environmental and health applications. Therefore, developing PNAs with high enhancement over a wide frequency range is highly desirable. Currently, the main way to solve the problem is to increase the bandwidth of PNAs by the combination and modulation of multiple resonances. A common approach of resonance combination is using a multi-resonance metasurface\(^{[12,20]}\) or supercell\(^{[21]}\) design to excite multiple adjacent resonances for the bandwidth in the mid-infrared region. Similarly, pixelated arrays can also ob-
Figure 1. Design principles and main results of our designed PNAs. a) Schematic of the designed PNAs. From bottom to top: Si substrate (gray), Au film (yellow), MgF$_2$ dielectric spacer layer (blue), Au nanoantennas (yellow). PNAs with different coupling modes can be obtained by tuning the loss of the coupling system realized by changing the thickness of MgF$_2$. The inset represents 13 analytes, including chlorpyrifos (CPF), inositol (In.), creatinine (Cr), chloramphenicol (CPL), tetracycline (TC), methylene blue (MB), Zeolitic Imidazolate Framework-8 (ZIF-8), polyethyl cyanoacrylate (PECA), o-Phenanthroline (o-phen), 2-Mercaptobenzimidazole (MBI), Safranine T (ST), Vitamin C (VC), and Rhodamine 6G (R6G). b) Theoretical model. Coupling modes are determined by the relationship between $\gamma_r$ and $\gamma_a$. OC: $\gamma_r > \gamma_a$ (namely, $\gamma_r/\gamma_a > 1$). UC: $\gamma_r < \gamma_a$. c) Calculated absorption spectra of PNAs for UC mode ($\gamma_r/\gamma_a = 0.3$, in blue) and OC mode ($\gamma_r/\gamma_a = 10$, in red). Solid curves: PNAs with molecules. Dashed curves: bare PNAs. The gray-shaded area is the molecular absorption spectrum. DF is defined as the detuning corresponding to when the global maximum enhancement intensity decays to $1/e$. Large DF means that PNAs can still greatly enhance the molecular signal in the strongly detuned state. That is, PNAs with larger DF can achieve stronger spectroscopic sensing in a wider band. d) Demonstration of PNAs at strong OC modes for the broad spectral analysis and identification of 13 kinds of molecules with the help of machine-learning. e) Comparison of DF for various PNAs reported in previous and this work.
loss rates have large DF and can overcome the limitation of low enhanced signal in the strongly detuned state. We demonstrate that the DF of the OC-PNAs can reach 248 cm$^{-1}$, which is 173 cm$^{-1}$ wider than the widely used UC mode. The OC-PNAs show a low Q-factor resonance, which allows indiscriminate enhancement of abundant molecular fingerprints in a broadband spectral region (6–14 μm). Additionally, the molecular signals obtained by OC-PNAs are immune to the perturbation of the asymmetric Fano lineshape, and the natural absorption feature of molecules can be read directly without quadratic fitting. Preserving the light-matter coupling efficiency and immunity to spectral distortions in the ultra-broadband range allows single OC-PNAs to achieve spectral multiplexing and molecular fingerprint retrieval in the mid-infrared range. In the proof-of-concept demonstration, we propose a machine-learning approach for broad-spectrum analysis and precise molecular identification. It is described that molecular recognition from 13 molecules with vibration fingerprints strongly detuning with OC-PNAs shows a 100% identification accuracy.

2. Results and Discussion

2.1. Design Principles of the OC-PNAs Sensing Platform

The concept of the OC-PNAs sensing platform is shown in Figure 1. Here, OC-PNAs adopt the classic metamaterial absorber (MA) design scheme, that is, a metal-insulator-metal three-layer structure.[31] This is because MA has one more degree of freedom in thickness tuning than single-layer PNAs, making it easier to tailor and realize various light-matter interactions. As shown in Figure 1a, the MA consists of a gold nanoantenna on top, a customizable magnesium fluoride (MgF$_2$) dielectric layer, and a thin gold film on the bottom. Since the bottom gold film is optically opaque (thickness > 100 nm), the relationship between absorbance $A$ and reflectance $R$ can be simplified as $A = 1 - R$. When infrared light is vertically incident, MA can focus the incident light on the tip of the nanoantenna, providing strong light-matter interaction. Enhanced light-matter interactions can bridge the gap between infrared wavelengths (micrometer scale) and molecular analyte sizes (nanometer scale), revealing chemically specific absorption bands for trace analytes.[5,9] Traditionally, the MA design strategy is to suppress the radiative loss of the system and increase the absorptive loss.[27,28] In this case, the obtained MAs are usually in CC and UC modes, and the absorption spectra exhibit narrow-band and high-Q characteristics.[27,28,32,33] (see dashed line in Figure 1cii). To obtain observable intensity changes, it is often necessary to tailor the resonant frequency of the nanoantenna to spectrally overlap with the characteristic vibrational mode of the target molecule. However, the characteristic fingerprints of molecules are complex and diverse in the mid-infrared range, and narrow-band plasmon resonances cannot match more fingerprint vibrations. The result is a weakening of molecular vibrations away from the plasmon resonance (see solid line in Figure 1cii). To address this issue, we calculated the complete spectral response of the plasmonic-molecular coupling based on TCMT. Detailed calculation and analysis will be carried out in the next section. Through calculations, we found that increasing the radiative loss while suppressing the absorption loss yields an absorption spectrum with a low-Q and broadband (shown as the dashed line in Figure 1cii). In this case, the MA is in OC mode, and the corresponding nanoantennas are called OC-PNAs. Broadband absorption spectroscopy enables OC-PNAs to maintain strong sensitivity even when spectral detuning, thereby opening up exciting opportunities to detect multiple fingerprint vibrations of molecules (see solid line in Figure 1cii).

In addition to bandwidth, we also found that the OC mode is immune to spectral distortion. Spectral distortion refers to the inconsistency between the acquired detection signal and the natural absorption characteristics of the analyte, manifested as an asymmetric Fano-type or more complicated lineshapes. To date, spectral distortions have been commonly observed in a plasmonic-molecular coupled system,[18,34] as shown by the blue curve in Figure 1c. The spectral distortion is related to the Fano resonance, which is attributed to the strong interaction between the molecular dipole and the plasmonic mode of the absorber resonance.[22] The coupling between plasmonic and molecular vibrational modes results in a modification of the spectral lineshape and a shift in the resonance frequency. Depending on the energy detuning and loss rate of the coupled system, the induced Fano resonances usually manifest in three types: quasi-Lorentz, asymmetrical, and Lorentz.[35] Among them, the spectral disturbance caused by the asymmetric Fano lineshape seriously hinders the correct reading of molecular vibration frequency, bandwidth, and intensity.[36] Although some works have been reported to extract molecular natural vibration frequencies from asymmetric spectra through Fano formula fitting,[34] they are still intractable when dealing with the multi-fingerprint vibration problem. Therefore, eliminating or weakening the asymmetric Fano lineshape is crucial to accurately obtain molecular information. Fortunately, the detection signal in OC mode is not affected by the spectral detuning and can maintain the Lorentz lineshape in the mid-infrared range, as shown by the red curve in Figure 1c. The Lorentz lineshape is consistent with the natural absorption characteristics of the molecule, and the chemical structure information of the molecule can be obtained without quadratic fitting.

Molecular fingerprint retrieval was realized by utilizing the broadband enhancement and spectral distortion immunity properties of MA in OC mode. In the experiment, we enhanced the radiative loss of the resonator by increasing the thickness of MgF$_2$ (h) and tuned the MA into the OC mode. Here, we selected 13 kinds of molecules to be sequentially coated on the surface of MA through non-specific binding to verify the molecular fingerprint retrieval. These molecules include chlorpyrifos (CPF), inositol (In.), creatinine (Cr.), chloramphenicol (CPL), trimethylamine (TC), methylene blue (MB), zeocin imidazole framework-8 (ZIF-8, polyethyl cyanocrylate (PECA), o-phenanthroline (o-phen), 2-mercaptopenimidazole (MBI), safarine T (ST), vitamin C (VC), and rhodamine 6G (R6G) (Figure 1a). We proposed to use principal component analysis (PCA) and support vector machines (SVM) algorithms to realize molecular fingerprint retrieval, as shown in Figure 1d. A set of spectral data from MA for different analytes was selected as input to the machine-learning algorithm. Different principal components (PCs) were identified through feature extraction via PCA. Then the SVM algorithm is used to classify the data in the PC domain. Finally, the classification and identification of 13 analytes were realized.
To fully understand light-matter interactions, we use the TCMT model to analyze plasmonic-molecular coupling systems. Based on TCMT, we can obtain the equation for the MA-molecular coupling system and extrapolate to the absorption spectral dispersion as (detailed derivation is shown in Note S2, Supporting Information),

\[
A = 1 - \left| \frac{k^2}{j(\omega - \omega_0) + (\gamma_r + \gamma_a) + \left( \frac{\mu^2}{j(\omega - \omega_0) + \gamma_a} \right)} \right|^2 \tag{2}
\]

where \(\omega_0\) and \(\omega_a\) are the resonance frequencies of MA and molecular vibration. \(\gamma_r\) and \(\gamma_a\) represent the radiative and absorptive losses of MA, while \(\gamma_i\) represents the absorptive loss of molecules. \(k\) is the coupling coefficient between light and MA \((k = \sqrt{2k_f})\). \(\mu\) is the coupling coefficient between MA and molecules. The detection signal spectrum \(|A|\) is defined as the difference in the absorption spectra with \(|A|\) and without \(|A|_{\mu=0}\) the molecule,

\[
\Delta A = |A| - |A|_{\mu=0} \tag{3}
\]

To observe the signal enhancement at the molecular vibration frequency \(\omega_{\mu=0}\), we define \(\Delta A|_{\omega=\omega_{\mu=0}}\) as the sensitivity of plasmonic sensors. Based on the above theory, we calculated the sensitivity image of MA as the normalized spectral detuning \(\delta = (\omega_a - \omega_{\mu=0})/\omega_{\mu=0}\) and \(\gamma_r/\gamma_a\), as shown in Figure 2a. The detailed parameter settings are shown in Table S1 (Supporting Information). In addition, we comprehensively calculate and discuss the generalized rules of molecular signal enhancement in PNAs (Note S3 and Figure S2, Supporting Information). Theoretical calculations show that MA has stronger sensing sensitivity than single-layer PNAs.

Next, we use numerical simulation to verify the above theoretical calculation results (See Note S4, Supporting Information, for detailed parameters of MA). Through simulation analysis, we understand the relationship between the loss rate of MA and the thickness of the dielectric layer (Figure S3, Supporting Information). In particular, there is an opposite change between \(\gamma_r\) and \(\gamma_a\) as the thickness of the dielectric layer increases. When \(h < 200\) nm, \(\gamma_r < \gamma_a\), MA is in UC mode; when \(h = 200\) nm, \(\gamma_r = \gamma_a\), MA is in CC mode; when \(h > 200\) nm, \(\gamma_r > \gamma_a\), MA is in OC mode. The resonance wavelength of the nanoantenna is positively correlated with the length of the antenna (Figure S4, Supporting Information). Furthermore, the numerical simulation results of the molecular enhanced signal are obtained (Figure S5, Supporting Information), which are consistent with the theoretical calculation results. Based on the simulation results, a series of MAs with different \(\gamma_r/\gamma_a\) and resonance frequencies were fabricated using a complementary metal-oxide-semiconductor (CMOS) compatible process (Figure S6, Supporting Information). Scanning electron microscope (SEM) characterization shows that the nanoantenna structures are clear, and the different layers adhered tightly (Figure S7 and Table S2, Supporting Information). The loss rates of MA devices were fitted by the TCMT model, which was \(\gamma_r/\gamma_a \approx 0.33\) (UC mode), \(\gamma_r/\gamma_a \approx 0.73\) (UC mode), and \(\gamma_r/\gamma_a \approx 4.4\) (OC mode) (Figure S8 and Table S3, Supporting Information). A ZIF-8 film of the same thickness was deposited on the surface of the device as the enhancement molecule (Figure S9, Supporting Information). Material characterization shows that the ZIF-8 deposited by our method is uniformly distributed on the antenna surface (Figure S10, Supporting Information). Detailed spectral measurement results are shown in Figures S11 and S12 (Supporting Information).

In Figure 2a, we can intuitively find the general rules and optimal parameter configurations applicable to all MA molecular sensors, which are very important for practical applications. Previous studies have shown that even the low-Q OC mode has the same magnitude of signal enhancement as the UC mode \([24]\) (Figure 2b,c), which provides exciting opportunities to exploit the sensing properties of OC modes. The only difference is that the peak positions of the two are opposite. This difference originates from two quantum coherent effects under light-dark coupling, namely the electromagnetically induced transparency (EIT) \([37]\) and electromagnetically induced absorption (EIA) \([38]\) effects. Both effects are related to the phase of the coupled system. According to the coupled mode theory, the radiation phase spectrum \(\varphi\) of the MA can be expressed as follows,

\[
\varphi = \text{phase}\left(\frac{S_{\text{max}}}{S_{\text{min}}}\right) = \left(\frac{\omega_0 - \omega_{\mu=0}}{j(\omega - \omega_0) + (\gamma_r + \gamma_a)}\right)
\]

where \(r_0\) represents the reflection coefficient of MA. According to Equation (4), we calculated the radiation phase spectra at \(\gamma_r/\gamma_a\) of 0.33 and 4.4, as shown in Figure 2e. The resonance frequency of MA is 1150 cm\(^{-1}\). A significant phase lag (with a lag magnitude of 180°) is found at the resonance point when the coupled mode transitions from UC to OC \([19]\). The phase lag in the plasmonic-molecular coupled system transforms the destructive interference into constructive interference, thereby inducing the signal response to realize the transition from EIT to EIA. Interestingly, the CC mode (CC mode is also often referred to as a metamaterial perfect absorber due to its close to unity absorption) is exactly in the transition region from EIT to EIA. The unique position of the CC mode causes its signal strength to approach zero at spectral matching. Therefore, to obtain a stronger detection signal, it should be avoided to design the MA in CC mode. In addition, we also observe an interesting phenomenon that the near-OC mode has two local maxima at spectral detuning (Figure 2bii). This phenomenon has also been observed in the transmission spectra of signal-layer PNAs (Figure S2e, Supporting Information) \([29]\).

In addition, we found that the OC mode is less affected by detuning, which can be obtained by comparing the width of the red and blue regions, as shown in Figure 2a. Here, we calculated the contour lines when the sensitivity decays to 1/e of the global maximum value (corresponding to 8.2% and –8.2% in Figure 2a, \(I_{\text{max}} = 22.3\%\)), for intuitive comparison of DF under different \(\gamma_r/\gamma_a\). Theoretical calculations show that the DF of the UC mode (blue area) is generally restricted to a small range. Under this constraint, strict spectral matching is adopted in the UC mode to enhance the sensing sensitivity. However, several factors challenge the strict matching of spectra, including the refractive indices of free space and analytes, as well as design and process variations. Conversely, the DF of the OC mode increases with an increasing...
Figure 2. Effects of spectral detuning and $\gamma_r/\gamma_a$. a) Calculated 2D mapping (TDM) of enhanced molecule signals as a function of normalized spectral detuning rate ($\delta$) and $\gamma_r/\gamma_a$ (see Note S3, Supporting Information, for detail). The y-axis uses a logarithmic scale. Contour lines with signal strengths of $-8.2\%$, $0\%$, and $8.2\%$ are displayed. The signal strength of $8.2\%$ is calculated when the global maximum enhancement strength ($I_{\text{max}} = 22.3\%$) decays to $1/e$. The purple-, red-, and blue-dashed lines are the parameters of fabricated MA with different $\gamma_r/\gamma_a$, respectively. The inset shows a schematic of the MA structure. In the experiments, the $\gamma_r/\gamma_a$ was tuned by changing the thickness of the dielectric layer, and the spectral detuning was tuned by changing the length of the cross-shaped nanoantenna. b) Measured molecule signal for MA with different $\gamma_r/\gamma_a$ as a function of spectral detuning (points), fitted with theoretical predictions (dashed lines). c) Measured dependence of the enhanced molecule signals on the loss rate of MA (points). Dashed lines show the theoretical prediction. d) Maximum absorption (gray), bandwidth (magenta), Q factor (blue), and maximum field enhancement (red) of MA as a function of $\gamma_r/\gamma_a$. e) Calculated radiation phase spectra when $\gamma_r/\gamma_a$ is $0.33$ (blue) and $4.4$ (red). The inset is a schematic diagram of phase lag-induced EIT conversion to EIA.

Taking OC with $\gamma_r/\gamma_a \approx 4.4$ as an example, its DF can reach $110 \text{ cm}^{-1}$, which is much larger than that of the UC mode. This difference can be understood because the OC mode has a larger bandwidth compared to the UC mode (Figure 1c). The corresponding full width at half maximum (FWHM) was calculated, as shown in Figure 2d magenta curve. A larger FWHM is usually accompanied by a lower Q factor (Figure 2d blue curve). It should be emphasized that the molecular vibrational enhancement in the OC mode does not weaken with the decrease of the Q factor. This feature was also verified in experiments (Figure 2b,c; Figure S11, Supporting Information). Further, we obtained the near-field enhancement as a function of $\gamma_r/\gamma_a$ by simulation, as shown by the red curve in Figure 2d. It can be found that near-field enhancement reaches its maximum value in OC mode. In addition, as the thickness of the dielectric layer increases, the electric field is transferred from the interior of the dielectric layer to the tip of nanoantennas (Figure S7c, Supporting Information). The electric field shift and huge near-field enhancement in OC...
Figure 3. Disappearance of anticrossing behavior in MA. a–c) Calculated TDM of the absorption difference spectra as a function of spectral detuning at $\gamma_r/\gamma_a$ of 0.33, 0.73, and 4.4. Gray line denotes the 1150 cm$^{-1}$ vibrational band of molecule. The black-, red-, and blue-dashed lines represent the absorption difference spectra with detuning rates of 0, 0.02, and 0.08, respectively. Gray-shaded areas are coupled molecular vibrational spectra.

Figure 3 d–f) Measured TDM of the absorption difference spectra as a function of spectral detuning at MgF$_2$ thicknesses of 175, 200, and 650 nm. ZIF-8 is the detection molecule. Gray line denotes the 1147 cm$^{-1}$ vibrational band of ZIF-8 molecule. Correspondingly, the absorption difference spectra of the three detuning cases are extracted. The gray-shaded area is the partial vibration spectrum of ZIF-8 molecule, which is used for comparison with the absorption difference spectra.

mode also mean that it is more competitive than CC or UC mode in molecular sensing.

2.3. Disappearance of Anticrossing Behavior in MA

$\gamma_r/\gamma_a$ and detuning rate of plasmonic resonators not only affect the enhancement sensitivity, but also control the evolution of the molecular enhanced spectral lineshape. To demonstrate this intuitively, we theoretically calculated the absorption difference spectra as a function of the detuning rate (Figures S13 and S14, Supporting Information). Figure 3a–c extracts images of the absorption difference spectra in three coupling modes, which correspond to UC ($\gamma_r/\gamma_a$≈0.33, Figure 3a), near CC ($\gamma_r/\gamma_a$≈0.73, Figure 3b) and OC ($\gamma_r/\gamma_a$≈4.4, Figure 3c), respectively. Among them, a clear anticrossing behavior is observed when $\gamma_r/\gamma_a$≤1. The anticrossing behavior covers all cases of Fano resonances,$^{[32,33]}$ which can be found in the extracted absorption difference spectra. In particular, when the plasmon resonance is slightly mismatched with the molecular vibration, the absorption difference spectra present asymmetric Fano lineshape, as shown in the red curves in Figure 3a,b. Compared with the natural vibrational state of the molecule (Figure 3a,b gray-shaded area), the asymmetric Fano lineshape will cause additional frequency shift and lineshape distortion. This spectral distortion poses challenges for the accurate interpretation of measured spectra and quantitative analysis. In UC and CC modes, there are two ways to weaken the effect of asymmetrical Fano lineshape. A common
approach is to tailor the resonant frequency of the device to match the vibration of the molecular fingerprint. In this case, the acquired absorption difference spectrum presents a quasi-Lorentz lineshape (Figure 3a,b black curves). The quasi-Lorentz lineshape is a product of the EIT effect, and its resonance direction is opposite to the classical Lorentz lineshape. Another way is to make the resonant frequency of the device far away from the molecular fingerprint vibration frequency, in which case the absorption difference spectrum exhibits a Lorentz lineshape (Figure 3a,b blue curves). However, this approach comes at the expense of detection sensitivity.

Interestingly, the system loss provides a new dimension in controlling spectral lineshape. When \( r/\gamma \) is increased to the OC mode, the anticrossing behavior disappears (Figure 3c). The disappearance of the anticrossing behavior indicates that the absorption difference spectra exhibit Lorentz lineshape, regardless of the detuning rate, as shown by the curves in Figure 3c. It should be emphasized that the disappearance of the anticrossing behavior does not imply a decrease in sensitivity, which has been confirmed in Figure 2. Unlike the UC and CC modes, when the plasmon resonance is matched to the molecular vibration, the absorption difference spectrum exhibits a Lorentz lineshape (related to the EIA effect). This difference avoids the switching of the absorption difference spectrum from the quasi-Lorentz lineshape to the Lorentz lineshape during the detuning process, thus maintaining the Lorentz lineshape in the mid-infrared range. Furthermore, observable sensitivity can still be obtained from the OC mode even under strong detuning conditions (shown by the blue curve in Figure 3c), which is consistent with the broadband enhancement described in Figure 2. Similarly, simulations (Figure S15, Supporting Information) and experiments (Figure 3d–f) also verified the disappearance of the anticrossing behavior. Experimentally, we assigned MAs to different coupling modes by controlling the dielectric layer thickness (Table S3, Supporting Information). A ZIF-8 film of the same thickness is deposited on the device surface (Figure S10, Supporting Information). For simplicity, we only show the absorption difference spectrum at 1147 cm\(^{-1}\). It is intuitively found that the anticrossing behavior gradually disappears as the thickness of the dielectric layer increases. Note, the disappearance of the anticrossing behavior is attractive. It implies that the OC mode can be easily extended to quantitative analysis and complex fingerprint recognition applications.

### 2.4. Strongly Detuned Sensing Demonstration of OC-PNAs

Based on loss engineering, we demonstrate the potential advantages of OC mode for plasmonic-molecular coupling spectroscopy. Next, we further explore the MA’s performance in strong OC mode. It can be found from Figure 2a that a larger DF can be obtained as \( r/\gamma \) continues to increase. In particular, theoretical calculations show that the DF of \( r/\gamma = 10 \) (strong OC mode) is 40 cm\(^{-1}\) wider than that of \( r/\gamma = 4.4 \). Although the sensitivity of the strong OC mode at spectral matching is slightly decreased compared to \( r/\gamma = 4.4 \), this loss can be traded for better sensing performance under strong spectral detuning. We further experimentally verify the ultra-wideband enhancement properties of the strong OC mode (Figure 4). In Figure 2, we achieve modulation of \( r/\gamma \) by modifying the thickness of the dielectric layer. However, the huge dielectric layer thickness presents process and cost challenges when constructing a strong OC mode. Furthermore, depending on the material, thicker dielectric layers may introduce additional inherent losses in the absorption spectrum. In addition to modifying the dielectric layer, optimization of the antenna structure and cell period can also achieve modulation of \( r/\gamma \). Therefore, we fixed the thickness of the dielectric layer to 500 nm and obtained the structure design of \( r/\gamma = 10 \) by reducing the unit cell period (2.5 \( \mu \)m) and changing the antenna structure (square with a side length of 2.05 \( \mu \)m). The device characterization is shown in Figure 4a.

In UC, OC, and strong OC modes, MAs with the same resonant frequency were selected for comparison. ZIF-8 films of the same thickness were deposited on the surfaces of the three MAs, and the experimental spectra are shown in Figure 4b. Figure 4c shows the absorption difference spectra using the asymmetric least squares smoothing (AsLSS) algorithm. Due to the ultrabroadband enhancement of the strong OC mode, we can obtain more vibrational modes of ZIF-8 from the absorption difference spectrum (Figure 4c). Compared with traditional methods of inserting or modulating resonance peaks, PNAs with strong OC mode can identify complex molecular compounds and structures in a single-pixel modulation-free manner.

Next, we demonstrate the capability of our PNAs in strong OC mode for quantitative detection and multi-fingerprint detection. We deposited ZIF-8 films of different molecular weights on the device surface, and the measured absorption spectra are shown in Figure 4d. Obviously, the molecular vibrational fingerprint is gradually enhanced with the increase of soaking times. In addition, due to the influence of the load refractive index, the absorption spectra exhibit a red-shift effect. However, decoupling the load-dependent refractive index changes by evaluating the redshift is challenging due to complex fingerprint vibrations. Thus, we introduce a third-order vibrational mode with high Q. High-Q third-order vibrational mode of the strong OC mode can be used for sensitive refractive index sensing, which is complementary to the fingerprint sensing of the first-order vibrational mode. Further, the absorption difference spectra were extracted by the AsLSS algorithm (Figure 4e). Importantly, the absorption difference spectra in the strong OC mode are consistent with the natural fingerprint of ZIF-8, which is attributed to the immunity of the high \( r/\gamma \) to the asymmetric Fano resonance. This feature also makes the surface-enhanced infrared absorption (SEIRA) spectroscopy comparable to the relatively mature Surface-enhanced Raman spectroscopy, that is, the complex vibrational information of the detected object can be restored only by baseline correction. Finally, we extracted the detection sensitivity of the device as shown in Figure S16 (Supporting Information).

### 2.5. Molecular Identification by Machine-Learning

In PNAs applications, chemical identification and spectral multiplexing of plasmonic sensing platforms are crucial. However, conventional PNAs suffer from detuning, making it difficult to obtain rich fingerprint information in the mid-infrared range using a single PNA, let alone chemical identification. PNAs at strong OC modes could provide the possibility for...
Figure 4. Strong detuning characteristics and quantitative demonstration of OC-PNAs. a) SEM images of MA antenna structures and cross-sections at different $\gamma_r/\gamma_a$. False color has been used for better clarity in SEM images of antenna structures. The blue is the MgF$_2$ dielectric layer, and the yellow is the Au nanoantenna. Detailed loss parameters are extracted based on TCMT (Table S3, Supporting Information). b) Measured absorption spectra (solid curves) of the same thick ZIF-8 film on the different $\gamma_r/\gamma_a$ MA platforms. Calculated baseline (dashed curves) of the spectra based on the AsLSS algorithm. c) The baseline corrected spectra difference in absorption (b). d) Measured absorption spectra of OC-PNAs ($\gamma_r/\gamma_a = 10$) devices with different thicknesses of ZIF-8 films. The first-order resonance mode is used for broad-spectrum analysis, and the third-order resonance mode is used for refractive index sensing due to its high-Q. e) Extracted TDM of the absorption difference spectra as a function of ZIF-8 growth times. The pink-shaded area is the intrinsic fingerprint vibration peak of ZIF-8.

In addition to the ZIF-8 mentioned above, we also measured 12 analytes (Figure 5b), including CPF, In., CPL, TC, MB, PECA, o-phen, MBI, ST, VC, and R6G (see Figure S17, Supporting Information, for molecular intrinsic vibrational spectra). These analytes cover applications in a variety of fields, including biomedicine, chemical analysis, materials science, and environmental monitoring. Figure 5c extracts the molecular vibrational enhancement spectra of different species. Chemical identification is achieved by comparing the molecular vibrational enhancement spectrum to the known spectrum of the target chemical. However, this method is not necessarily optimal in terms of the accuracy of chemical identification and the time required to obtain an answer. Therefore, we use machine-learning algorithms to solve the problem of molecular recognition. First, the spectra of the OC-PNAs coated with different molecules were measured, each molecule containing 50 absorption spectra (Figure 5a). Then, the spectral data are classified by PCA, and the processing results are shown in Figure 5d–f. In Figure 5f, each cluster represents a type of molecule. Figure 5g–i are the projections of PCA on 3D space. Since each molecule does not overlap in space, we can identify different molecular species. In addition, we also demonstrated that OC-PNAs combined with SVMs were used to achieve 100% molecular recognition (Note S9 and Figure S18, Supporting Information). In contrast to the previous detection of a limited number of absorption peaks, our device can identify all fingerprint vibration modes in the 6–14 $\mu$m range. Furthermore, the fingerprint reduction property of the strong OC mode makes the SEIRA spectra compatible with existing infrared spectral databases, paving the way for sensitive molecular sensing and global fingerprinting.
Figure 5. Demonstration of molecular identification with multi-fingerprint sensing signal from OC-PNAs by machine-learning. a) The absorption spectra sensing data with different analytes states. b) A set of absorption spectra extracted from (a). c) The baselined corrected spectra difference in absorption (b). d) The machine-learning processed spectra of OC-PNAs after dimension reduction by PCA. e) Explained variance for PCA. f) The weight of scores of each spectrum in 3D space after PCA for OC-PNAs. Each cluster indicates one type of molecule. g–i) Projection of PCA in 3D space.

3. Conclusion

In summary, we propose a design strategy for breaking the constraints of spectral matching with OC-PNAs for spectral multiplexing and global molecular recognition. We comprehensively reveal the enhancement rules of plasmonic-molecular coupling systems based on loss engineering, laying a foundation for the further design of high-quality PNAs. Importantly, we find that the OC mode, which has been rarely discussed before, is extremely advantageous in molecular sensing, including the superior sensing performance in the detuned state (large DF) and the additional property of the full-spectrum Lorentz lineshape response. These advantages enable PNAs to enable a wide range of spectroscopic analysis and nondestructive reduction of fingerprint vibrational spectroscopy. We further optimized the PNAs to strong OC mode to maximize the DF in light-matter interactions. Experimentally, we obtain a DF of 248 cm$^{-1}$ in the strong OC mode, which is 173 and 52 cm$^{-1}$ wider than the UC mode and OC mode, respectively (See Note S10, Supporting Information, for details and comparison of DF). Huge DF provides
broad prospects for PNAS applications, including quantitative detection, multi-fingerprint information identification, and multispecies classification. Based on the massive spectral data collected by the OC-PNAs, we introduced a machine-learning algorithm and achieved the accurate identification of 13 analytes. Looking forward, utilizing the near-field enhancement generated by the nanogap will further optimize the sensing performance of OC-PNAs and realize monolayer detection. We believe that our demonstrated light-matter interaction enhancement based on OC-PNAs will provide new ideas for numerous applications for enhanced spectroscopy, quantum photonics, and nonlinear photonics.

4. Experimental Section

Numerical Simulations: A commercial software package (FDTD Solutions ver. 8.19, Lumerical) was used for numerical simulations. To improve simulation efficiency, periodic boundary conditions were used in the x and y directions, and perfect matching layer (PML) boundary conditions were used in the z-direction. The refractive index of MgF$_2$ was set to 1.38, and the complex refractive index of gold was taken from Palik et al. A 3D frequency-domain power monitor was used to simulate near-field distribution. All simulated spectra and their TDM were obtained using FDTD combined MATLAB (R2017b) program. The theoretical analysis of TCMT and its TDM were obtained by the MATLAB program. The 10 nm thick Cr adhesion layer was omitted in the simulation.

Device Fabrication: All devices were manufactured using CMOS-compatible processes. The detailed manufacturing process: i) cleaning and drying three low-resistance 6” silicon wafers; ii) 10 nm thick Cr and 100 nm thick Au films through magnetron sputtering sequence deposited on a Si wafer, where Cr was used as an adhesion layer to enhance the adhesion between the gold film and the Si substrate; iii) 175, 200, 500, and 650 nm thick MgF$_2$ were deposited on four wafers by electron beam evaporation; iv) 10 nm Cr and 100 nm Au were sequentially deposited on the MgF$_2$ layer; v) a uniform layer of photoresist was spin-coated on the surface of the device, and then an ultraviolet stepper photolithography machine and ion beam etching (IBE) technology were used to pattern the nanoantenna array; vi) finally, a layer of photoresist was spin-coated on the surface of the device to protect the device. These devices were stored in a dry and sealed environment before use.

Preparation of ZIF-8 Film: The ZIF-8 film was made by mixing the Zinc nitrate hexahydrate and 2-methylimidazole in a methanol solvent. The detailed synthesis processes are shown in Figure S9 (Supporting Information). The devices were immersed in acetone and ethanol for 3 min to completely remove the photoresist and contaminants on the surface of the devices and then dried with nitrogen. The cleaned devices were immersed in a mixed solution of 10 mL Zinc nitrate hexahydrate (2.5 mol L$^{-1}$, methanol solvent) and 10 mL 2-methylimidazole (2.5 mol L$^{-1}$, methanol solvent), and the solution was soaked at room temperature for 1 min. After immersion, the devices were immersed in methanol solution for 1 min and dried with nitrogen flow. The ZIF-8 films of different thicknesses were prepared by repeating the above process.

Spectroscopic Measurements: Fourier transform infrared (FTIR) spectrometer (IR Tracer-100, Shimadzu) was coupled with an infrared microscope of mercury cadmium telluride (A1M 900, Shimadzu) cooled by liquid nitrogen to collect the infrared spectra of the devices. The numerical aperture of the infrared microscope was set to 0.4, and the objective lens was 15x. The signal acquisition area was limited to a single 100 x 100 µm$^2$ array by the knife-edge aperture. The measured spectrum of the Au mirror was used as the background spectrum. Other parameter settings were a mirror speed of 40 kHz, a resolution of 4 cm$^{-1}$, and the average value was taken after 25 scans for each measurement.

Statistical Analysis: Each experimental spectrum was an average of 25 scans. The preprocessing of spectral data, baseline calibration, parameter fitting, molecular vibration signal extraction, data post-processing, and PCA were all completed by Origin (Origin-Lab Corporation, USA) software. The proposed SVM classifiers were developed on Python 3.6 using the scikit-learn package.

Apparatus: SEM (Carl Zeiss SIGMA 500, Germany) was used to characterize the device’s morphology. Film thickness analyses were performed by a commercial atomic force microscopy (Dimension Icon, Bruker Inc). The Bruker Quantax energy-dispersive X-ray spectroscopy (EDS) system with an XFlash silicon drift detector was used for EDS analysis of the ZIF-8 film. Infrared spectroscopy measurements were performed on an FTIR spectrometer (IRTracer-100, Shimadzu) coupled with an infrared microscope of mercury cadmium telluride (A1M-900, Shimadzu) with liquid nitrogen cooling. Photolithography was performed by Nikon i-line stepper NSR-2205 i-12D. A magnetron sputtering system (FHR.Micro.200, FHR Inc) was used to deposit Au and Cr layers. The SCIA Mill 200 of the SCIA system was used for the dry etching of nanostructures.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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detuning, electromagnetically induced absorption, light-matter interaction, loss engineering, plasmonic nanoantennas