

Supporting information

Anisotropic acoustic phonon polariton-enhanced infrared spectroscopy for single molecule detection

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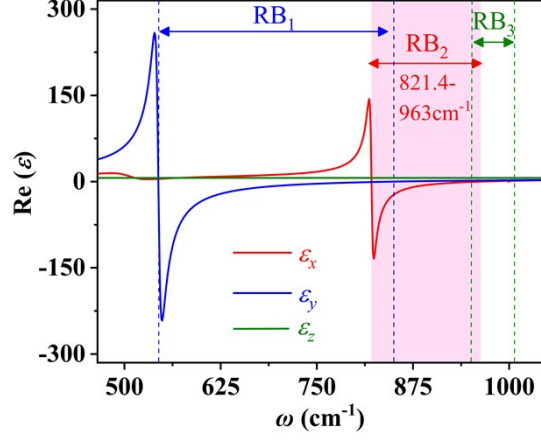


Fig. S1 The real part of the permittivity of α -MoO₃ in RB₂ is used in this study.

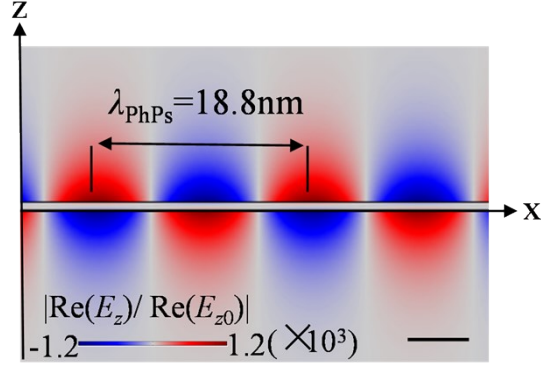


Fig. S2 Normalized electric field distribution $\text{Re}(E_z)/\text{Re}(E_{z,\text{PhPs}})$ of freestanding α -MoO₃ monolayer PhPs at $\omega = 880 \text{ cm}^{-1}$. The wavelengths of the PhPs are indicated by horizontal arrows. Scale bar: 5 nm.



Fig. S3 Side view of the layered structure of monolayer α -MoO₃/nano airgap/Au.

We calculate the dispersion of APhPs via the Fresnel reflection coefficient $r_p(q, \omega)$ method by modeling the sample as multilayer structure of monolayer α -MoO₃/nano airgap/Au.

The total reflectivity of this system is determined by following Equations:

$$r_p = \left(r_c + r_s e^{i2k_m^z d} \right) / \left(1 + r_c r_s e^{i2k_m^z d} \right) \quad (\text{S1})$$

$$r_c = \left(\epsilon_m \perp k_c^z - \epsilon_c \perp k_m^z \right) / \left(\epsilon_m \perp k_c^z + \epsilon_c \perp k_m^z \right) \quad (\text{S2})$$

$$r_s = \left(-\varepsilon_{m \perp} k_s^z + \varepsilon_{c \perp} k_m^z \right) / \left(\varepsilon_{m \perp} k_s^z + \varepsilon_{c \perp} k_m^z \right) \quad (\text{S3})$$

Where the subscripts “c”, “m” and “s” denote the α -MoO₃, air and Au, respectively. d is the thickness of the monolayer α -MoO₃. r_c and r_s represent the reflectivity of the α -MoO₃/air and air/Au interfaces, respectively. The $\varepsilon_{c \perp}$, $\varepsilon_{m \perp}$ represent the out-plane dielectric functions of α -MoO₃ and air, respectively. k_i^z is momentum component of the propagating wave along the z axis, which can be obtained by

$$k_i^z = \sqrt{\varepsilon_{i \perp} (\omega/c)^2 - \left[(\varepsilon_{i \perp} / \varepsilon_{i \parallel}) \cdot q^2 \right]} \quad (\text{S4})$$

Where $i = c, m$ and s , ω is the frequency of incident light, c is the speed of light in vacuum. $\varepsilon_{i \perp}$ and $\varepsilon_{i \parallel}$ represent the out- and in-plane dielectric functions of the corresponding i material. And the in-plane dielectric constant $\varepsilon_{i \parallel}$ of the α -MoO₃ is in the x direction (i.e., ε_{ix}).

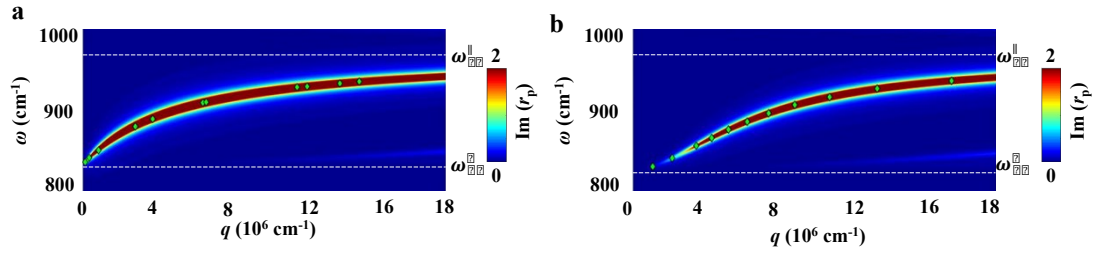


Fig. S4 (a) The dispersion relationship of PhPs in RB₂ by calculating the Fresnel reflection coefficient $r_p(q, \omega)$ of monolayer α -MoO₃ (false-color image) and the finite element method (FEM) simulation with COMSOL (green dots). **(b)** The dispersion relationship of APhPs in RB₂ by calculating the Fresnel reflection coefficient $r_p(q, \omega)$ of monolayer α -MoO₃/Au heterostructure (false-color image) and the finite element method (FEM) simulation with COMSOL (green dots).

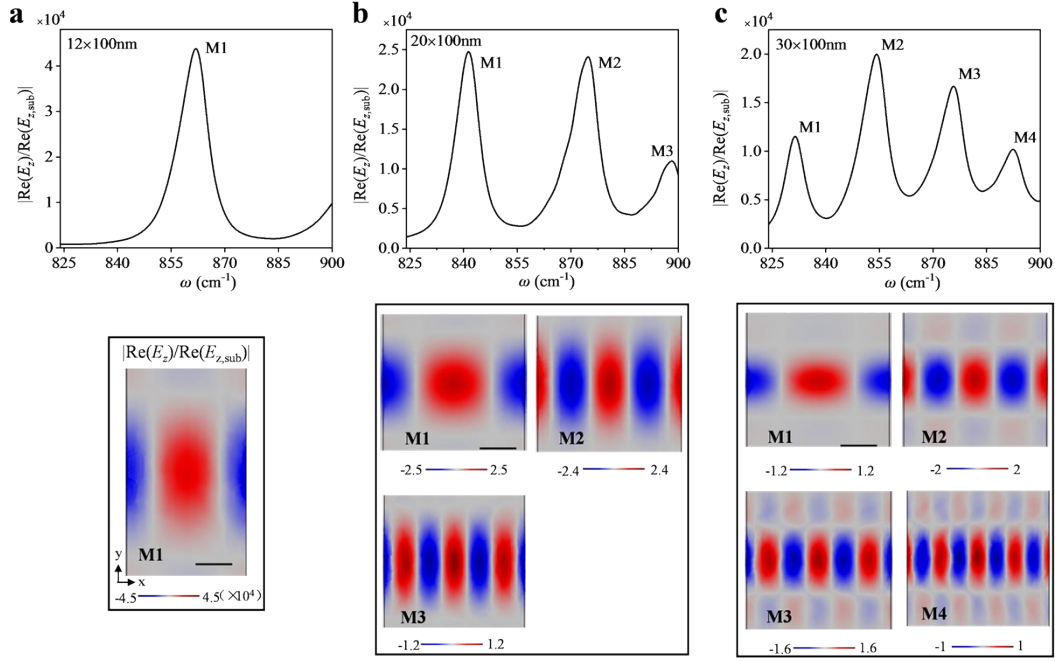


Fig. S5 (a) Top: Normalized electric-field spectra $|\text{Re}(E_z)/\text{Re}(E_{z,\text{sub}})|$ of APhPs in 12×100 nm monolayer α -MoO₃. Bottom: The electric field distribution of the M1 order mode of APhPs. The electric field cross-section is taken from 0.1 nm below α -MoO₃ at $\omega = 862$ cm⁻¹. Scale bar: 5 nm. (b) Top: Normalized electric-field spectra $|\text{Re}(E_z)/\text{Re}(E_{z,\text{sub}})|$ of APhPs in 20×100 nm monolayer α -MoO₃. Bottom: The electric field distribution of the M1 ~ M3 order modes of APhPs. The electric field cross-section is taken from 0.1 nm below α -MoO₃ at $\omega = 862$ cm⁻¹. Scale bar: 5 nm. (c) Top: Normalized electric-field spectra $|\text{Re}(E_z)/\text{Re}(E_{z,\text{sub}})|$ of APhPs in 30×100 nm monolayer α -MoO₃. Bottom: The electric field distribution of the M1 ~ M4 order mode of APhPs. The electric field cross-section is taken from 0.1 nm below α -MoO₃ at $\omega = 862$ cm⁻¹. Scale bar: 5 nm.

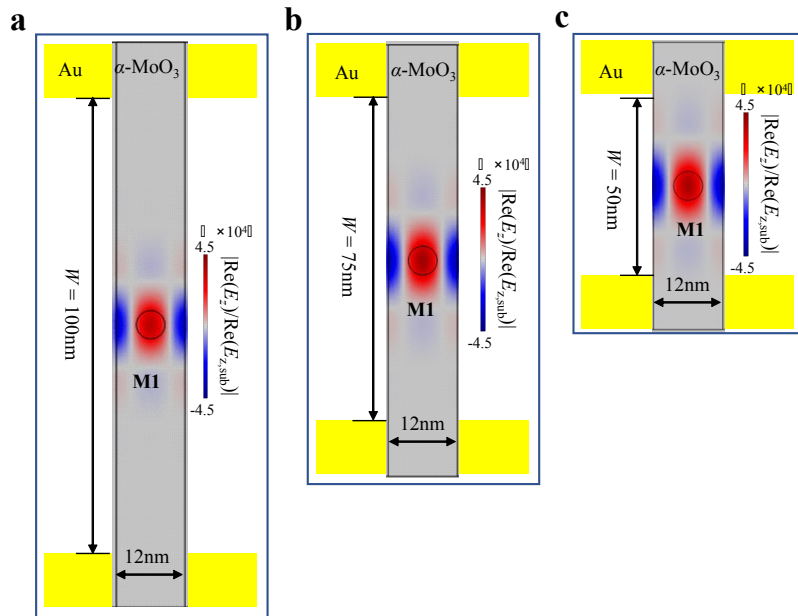


Fig. S6 (a, b, c) The corresponding APhPs field distribution when the size of α -MoO₃ in y-direction

becomes 100, 75, 50nm respectively. There are no-APhPs exist in the y-direction of dimensional change. The black circle indicates the position where the single molecule to be detected will be placed. The electric field cross-section is taken from 0.1nm below α -MoO₃ at $\omega = 862 \text{ cm}^{-1}$.

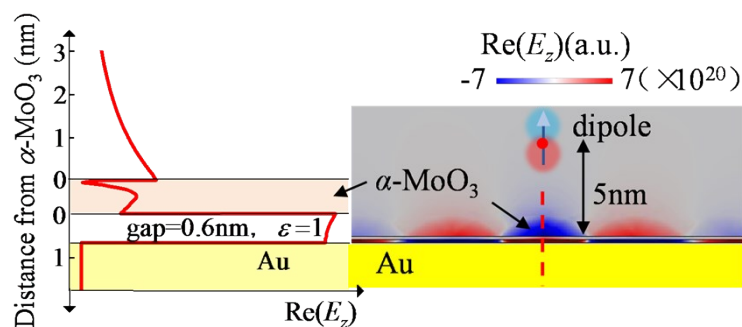


Fig. S7 Left: Numerical calculation results of the electromagnetic field distribution $\text{Re}(E_z)$ from the α -MoO₃ in the z-direction at 820 cm^{-1} . The value is derived from the red dashed line in the figure on the right. gap = 0.6 nm, $\epsilon = 1$. Right: Simplified side-view schematic of the electric field distribution of APhPs in the s-SNOM measurement. The atomic force microscope (AFM) tip is approximated using a simple electric dipole point-source. The dipole is 5 nm above the α -MoO₃ monolayer.

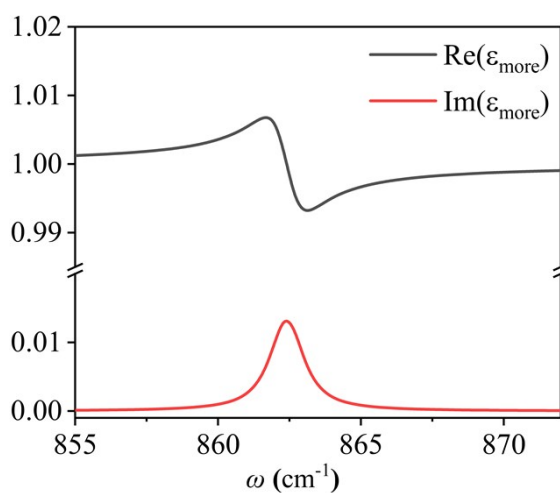


Fig. S8 Real part (black curve) and imaginary part (red curve) of the permittivity of molecule in the frequency range of interest.

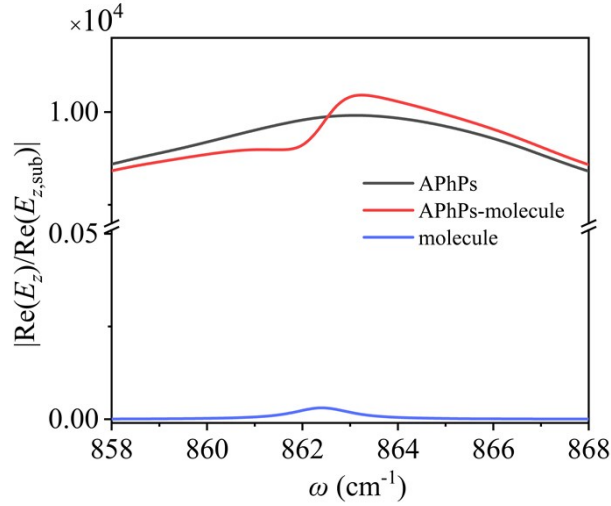


Fig. S9 Normalized electric-field spectra $|\text{Re}(E_z)/\text{Re}(E_{z, \text{sub}})|$ of APhPs in infinite $\alpha\text{-MoO}_3/\text{Au}$ heterostructure for enhancement of the molecular vibration (~ 3 -folds). APhPs and molecule coupling display a dip feature (red solid curve) and the bare molecule signal spectrum (blue solid curve).

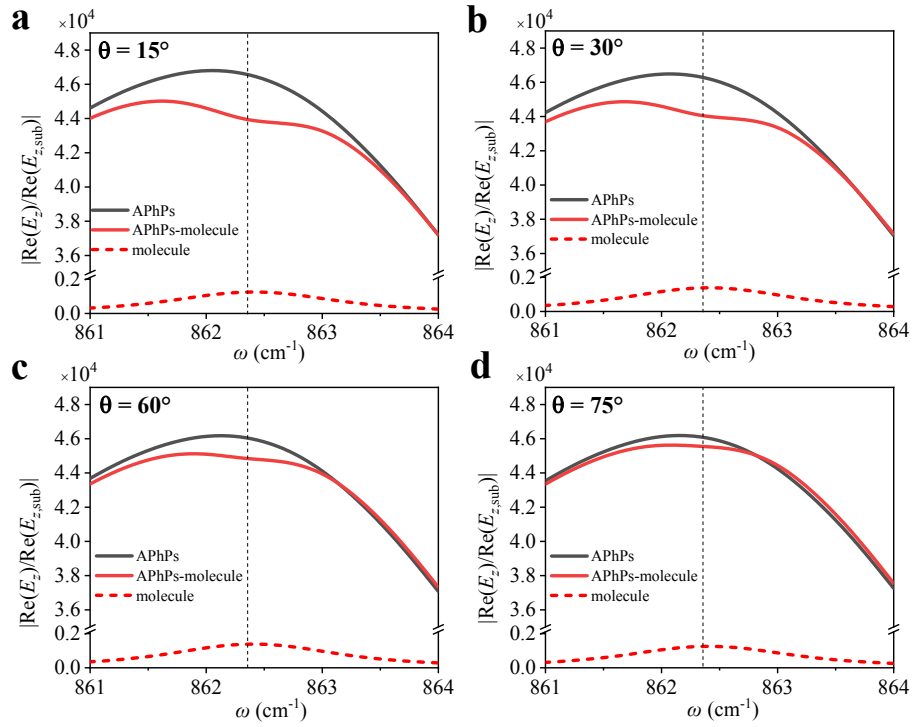


Fig. S10 (a, b, c, d) Normalized electric-field spectra $|\text{Re}(E_z)/\text{Re}(E_{z, \text{sub}})|$ of APhPs when the angle θ between the molecular dipole orientation and the APhPs propagation direction is 15° , 30° , 60° , and 75° . The coupling spectrum of APhPs and molecule (red solid curve), and the spectrum of molecule signal with enhancement 200-folds (red dashed curve).