

1 Nanoscale Spectroscopy of Dielectric Properties of Mica

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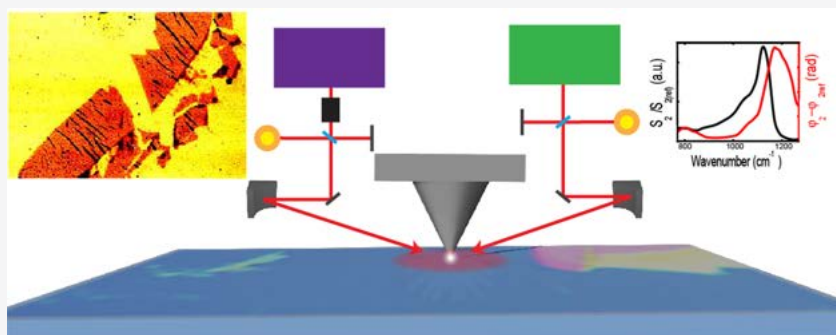
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4 **ABSTRACT:** Infrared dielectric properties of muscovite mica, one of the first van der Waals crystals, exfoliated on silicon and SiO₂
5 substrates is studied using near-field nano-FTIR spectroscopy. The spectra of mica show strong thickness and wavelength
6 dependence down to the monolayer-scale, with a prominent broad peak centered around $\sim 1080\text{ cm}^{-1}$ assigned to stretching
7 vibrations of Si–O. We reveal that the infrared dielectric permittivity of mica is anisotropic, that is, has opposite signs along the in-
8 plane and out-of-plane axes, implying a Type I hyperbolic behavior in the range $920\text{--}1010\text{ cm}^{-1}$ and a Type II hyperbolic behavior
9 in the range $1050\text{--}1130\text{ cm}^{-1}$. Experimentally measured nano-FTIR spectra agree well with analytical model calculations based on
10 an extended finite dipole model for layered systems of the tip–sample interaction when the out-of-plane dielectric values (instead of
11 the in-plane dielectric values) were used in the calculations.

12 **KEYWORDS:** hyperbolic materials, mica, 2D materials, nano-FTIR, van der Waals materials

13 **S**ince the isolation of monolayer graphene,¹ numerous other
14 layered materials have been identified.² These include,
15 transition metal dichalcogenides (TMDs) with the general
16 formula of MX₂, where M is a transition metal atom (e.g., M =
17 Mo, W, Ta, etc.) and X is chalcogen (e.g., X = Se, S, Te)
18 forming layers above and below M, hexagonal boron nitride,
19 and black phosphorus. In addition to providing a unique
20 platform to discover exciting new physics, layered materials are
21 promising for applications in flexible optoelectronics.³ While
22 the list of metallic and semiconducting 2D crystals is growing
23 by the day, the list of insulating 2D crystals is still limited.

24 Muscovite mica, with the chemical formula KAl₂(Al,Si₃)-
25 O₁₀(OH)₂, is among the earliest known van der Waals (vdWs)
26 materials that can be exfoliated in high quality to large sizes
27 ($>1\text{ cm}^2$) with atomic flatness.^{4,5} It can be prepared as a
28 monolayer through the exfoliation of natural muscovite.^{6,7} The
29 surface unit cell of bulk muscovite mica along the (001) crystal
30 plane harbors two K⁺ ions, when exfoliated (along the (001)
31 crystal face), only half the amount K⁺ ions per unit cell remain
32 to preserve surface charge neutrality. The K⁺ ions are tightly
33 locked in the interlayers, resulting in stronger interlayer force
34 in muscovite mica compared to the weak van der Waals forces
35 between layers in most other 2D materials. On the other hand,

the surface K⁺ ions exposed during exfoliation of muscovite
mica allow unique opportunities for novel surface chemistry
due to their ability to exchange with different cationic species
and ease of functionalization.^{8,9} Because the surface is
atomically flat, muscovite mica is an excellent substrate for
materials used in optoelectronics such as vdW flakes,⁷ self-
assembled monolayers,^{10–13} and light-emitting devices,^{14,15}
and is used as a template to produce the active layer in organic
solar cells.¹⁶ However, much of the optical properties of a
monolayer to few layer mica remain unexplored.

In this work, using a combination of mid-infrared scattering
type scanning near-field microscopy (s-SNOM) and nano-
FTIR, we perform near-field spectroscopy and imaging of 2D
crystal muscovite mica down to the monolayer limit.
Ellipsometry measurements enabled the extraction of the

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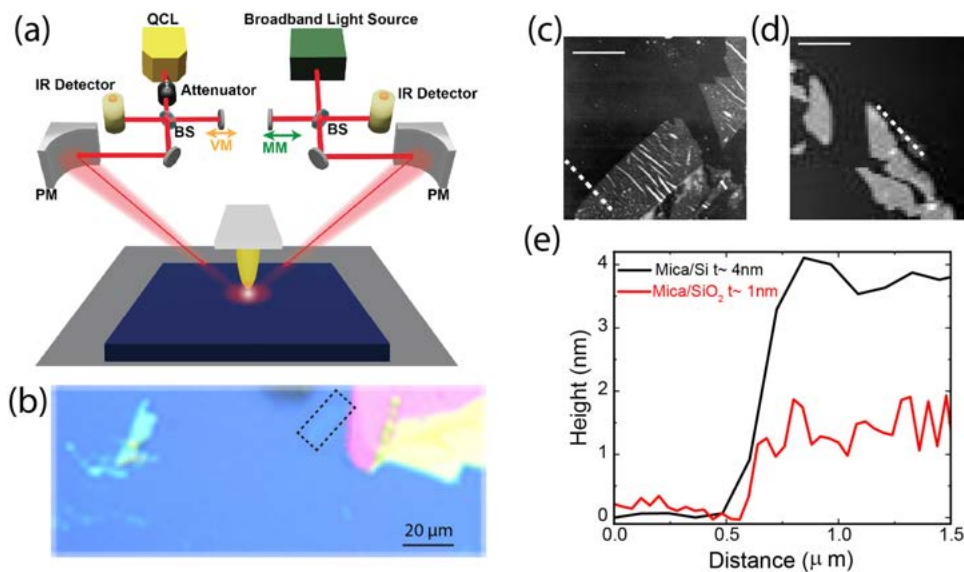


Figure 1. Optical micrograph and AFM topography images of exfoliated muscovite mica flakes. (a) Schematics of the nano-FTIR setup. (b) Optical image of exfoliated mica on SiO₂, Topography and of 4 nm thick mica on Si (c) and 1 nm thick mica on SiO₂ (d) and corresponding height line profiles (e). Scale bars in (c) and (d) are 1 μm.

51 dielectric function in this spectral range, highlighting that the
 52 infrared dielectric permittivity of mica along the ordinary and
 53 extraordinary directions have opposite signs in the 920–1130
 54 cm⁻¹ range, thus, implying regions of both Type I and Type II
 55 hyperbolic behavior. The thickness- and wavelength-dependent
 56 IR spectra of muscovite mica exfoliated on either Si or SiO₂
 57 substrates enabled sensitive detection spectra of mica down to
 58 the monolayer level, taking advantage of the SiO₂ phonon
 59 polariton enhanced resonant excitation. The in-plane and out-
 60 of-plane dielectric values of mica extracted from ellipsometry
 61 measurements were used to perform model calculations. Good
 62 agreement of theoretical calculations with experimentally
 63 measured nano-FTIR spectra were achieved when the out-of-
 64 plane dielectric values from ellipsometry measurements were
 65 used. With reduced loss, mica could provide a robust
 66 hyperbolic material for large-scale nanophotonics applications.

67 ■ RESULTS AND DISCUSSION

68 A commercially available mica sample was used for this study.
 69 We performed X-ray diffraction (XRD) measurements on the
 70 sample using a Rigaku Smartlab X-ray diffractometer equipped
 71 with a 9 kW Cu anode and collimating mirror producing Cu
 72 Kα quasi-parallel X-rays. The sample was mounted and aligned
 73 on an automated vertical goniometer, and diffraction spectra
 74 were collected using a 1d high sensitivity Si strip detector.
 75 XRD peak analysis and least-squares refinement were
 76 performed to obtain lattice constants, phase orientation, and
 77 average grain sizes. The mica sample was found to crystallize in
 78 the hexagonal, Muscovite 3T phase with space group: P3112.
 79 The sample is highly *c*-plane oriented with 7 orders of (00,*l*)
 80 reflections observed in the XRD spectra. The spectra also show
 81 that the sample has a high crystalline quality within the
 82 textured grains. The refined lattice parameters obtained were
 83 as follows: $a = 5.1948 \pm 0.0045$ Å and $c = 29.9735 \pm 0.0001$ Å.
 84 These XRD spectra and a table containing a list of the
 85 observed peaks, along with the indices, the computed peaks of
 86 the least-squares refined structure, and differences, as well as
 87 further XRD analyses can be found in Figure S1 and Table S1.

(c) (d)
 (e)
 Height (nm)
 Distance (μm)
 — Mica/Si $t \sim 4$ nm
 — Mica/SiO₂ $t \sim 1$ nm

A combination of s-SNOM and nano-FTIR is used to
 acquire topography, near-field images, and IR nanospectra on
 muscovite mica sample prepared by mechanical exfoliation on
 either Si or SiO₂ substrates. The experimental setup ((Figure
 1a, neaspec co.) is based on a tapping mode AFM with a
 cantilevered metal-coated tip that oscillates at a resonance
 frequency of $\Omega \sim 280$ kHz and a tapping amplitude of ~ 50
 nm. Either a coherent broadband infrared beam in the
 frequency range 700–2100 cm⁻¹ (for nano-FTIR) or a
 monochromatic IR laser (for s-SNOM) is focused by a
 parabolic mirror to the tip. For the nano-FTIR operation, the
 backscattered near-field light from the tip–sample junction is
 detected via mixing with an asymmetric Fourier transform
 Michelson interferometer. This detection method enables
 recording of both the amplitude $s(\omega)$ and the phase $\varphi(\omega)$
 spectra of the backscattered light. To extract background-free,
 local near-fields, the detector signal is demodulated at a higher
 harmonic $n\Omega$ of the tip mechanical resonance frequency Ω .
 Normalized amplitude ($s_n(\text{sample})/s_n(\text{reference})$) and phase
 ($\varphi_n(\text{sample}) - \varphi_n(\text{reference})$) IR near-field spectra are
 acquired by first taking the reference spectrum on a reference
 area (silicon is used in these experiments), followed by taking
 spectra at desired positions of the sample. Figure 1b shows a
 representative optical micrograph of mica flakes exfoliated onto
 a SiO₂ substrate, the rectangular box in black broken lines
 subtends a monolayer flake. Figure 1c,d shows AFM
 topography images of mica flakes on SiO₂ and Si, respectively.
 Red and black lines in Figure 1e are corresponding line profiles
 taken on dashed lines on the Si substrate (black line) and SiO₂
 substrate (red). While we could exfoliate a monolayer (height
 ~ 1 nm) flake on SiO₂ substrate,⁷ the thinnest flake we could
 exfoliate on Si had a height of ~ 4 nm.

The dielectric function of muscovite mica at mid-IR
 frequencies is necessary to understand its spectroscopic
 response, yet has not been reported previously. Thus, we
 performed ellipsometry measurements in the mid-IR frequency
 range, using an IR-VASE ellipsometer (J. A. Woollam Co.,
 Lincoln, NE). The substrate was mounted on a precision
 rotation stage, and a data set was acquired after the substrate

127 was rotated to 5 different rotational positions around the
 128 sample normal -0° (initial position), 45° , 90° , 135° , and 180° .
 129 Each data set included of data at incident angles of 45° , 60° ,
 130 and 75° . All data sets were acquired at a spectral resolution of 8
 131 cm^{-1} . After the measurement, the data were fit to a biaxial
 132 substrate model using standard numerical analysis methods
 133 similar to those described by Jellison^{17–19} and Herzinger.²⁰
 134 **Figure 2a,b** shows the real and imaginary parts of the dielectric

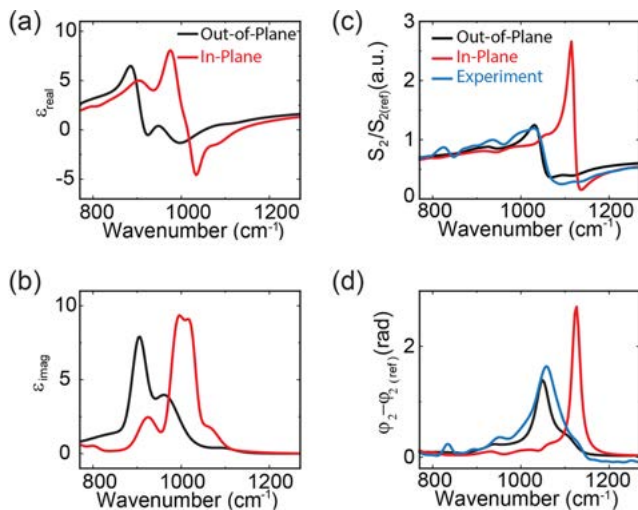


Figure 2. Ellipsometry and nano-FTIR spectra of muscovite mica. Mid-infrared dielectric function is extracted from far-field ellipsometry measurements of muscovite mica. Real (a) and imaginary (b) parts of the permittivity of the in-plane (red curves) and out-of-plane (black) components as a function of excitation frequency are provided. Extended finite dipole model calculation of near-field amplitude S_2 (c) and phase φ_2 (d) spectra performed by using the in-plane (red curves) and out-of-plane (black curves) permittivity. Nano-FTIR experimental spectrum taken on 40 nm mica flake on Si substrate is shown in blue in (c) and (d) for comparison.

135 functions, respectively, extracted from ellipsometry along the
 136 in-plane and out-of-plane directions (with respect to the
 137 sample plane). To produce the in-plane component of the
 138 dielectric function, we averaged the dielectric data for the in-
 139 plane X- and Y-axes values. This is because the difference
 140 between the X- and Y-axes dielectric data is insignificant (see
 141 SI, Figure S2) owing to polycrystalline (with z-axis aligned)
 142 nature of the sample. The real and imaginary permittivity
 143 values plotted in **Figure 2** for the in-plane (ϵ_i , red curve) and
 144 out-of-plane (ϵ_z , black curve) components clearly display
 145 anisotropy. Notably, $\text{Re}(\epsilon_z) < 0$, $\text{Re}(\epsilon_i) > 0$ in the frequency
 146 range $920\text{--}1010\text{ cm}^{-1}$ (excluding the range $930\text{--}955\text{ cm}^{-1}$)
 147 and $\text{Re}(\epsilon_i) < 0$, $\text{Re}(\epsilon_z) > 0$ in the frequency range $1050\text{--}1130$
 148 cm^{-1} . This implies that mica is a hyperbolic material (Type I in
 149 the range $920\text{--}1010\text{ cm}^{-1}$ and Type II in the range 1050--
 150 1130 cm^{-1}), this is because the in-plane and out-of-plane
 151 components of its dielectric permittivity have opposite signs in
 152 these frequency ranges. This behavior adds mica to the list of
 153 natural hyperbolic materials in the infrared.^{21–23} The
 154 imaginary parts of the permittivity curves shown in **Figure**
 155 **2b** represent dissipation of optical energy accompanying this
 156 anomalous optical hyperbolic behavior. These imaginary parts
 157 are relatively small in comparison with highly lossy metallic
 158 plasmonic materials, but are a factor of 271 at 800 cm^{-1} (Mica
 159 $\text{Im}(\epsilon_z)/\text{hBN Im}(\epsilon_z)$) and a factor of 32 at 1075 cm^{-1} (Mica
 160 $\text{Im}(\epsilon_z)/\text{hBN Im}(\epsilon_z)$) times larger compared to hBN, another

exfoliable hyperbolic material in the infrared.^{24,25} We note that
 the real part of permittivity ratio of mica to hBN is much
 smaller than the imaginary part ratio (0.38 at 800 cm^{-1} (Mica
 $\text{Re}(\epsilon_z)/\text{hBN Re}(\epsilon_z)$) and a factor of 0.04 at 1075 cm^{-1} (Mica
 $\text{Re}(\epsilon_z)/\text{hBN Re}(\epsilon_z)$) which implies an overdamped system.
 These experimentally acquired real and imaginary dielectric
 functions will be used to elucidate near-field spectra and
 hyperbolic response of mica, the role of thickness and
 substrate.

When the out-of-plane dielectric function is used in the
 extended finite dipole model, the calculated spectra fit
 experimental nano-FTIR spectra very well. This is evident in
Figure 2c,d, where the nano-FTIR experimental spectra (blue
 line) are compared with tip–sample near-field interaction
 analytical model calculations using the in-plane (red line) and
 out-of-plane (black line) dielectric data from **Figure 2a,b**. The
 normalized near-field nano-FTIR amplitude (**Figure 2c**) and
 phase (**Figure 2d**) spectra were acquired by taking broadband
 spectra on a 40 nm mica flake and normalized them to a
 spectra taken at a reference point on the Si substrate
 surface.^{26,27} The calculations were performed by modeling
 the tip–sample near-field interaction based on a multilayer
 finite dipole model²⁸ in which the tip is approximated as an
 ellipsoid of length of 600 and 30 nm apex radius. The tip is
 illuminated by the infrared beam at an angle of 30° relative to
 the sample plane and the scattered signal is collected by the
 detector, providing amplitude and phase spectra, $s_n(\omega)$ and
 $\varphi_n(\omega)$ ²⁹ via higher-harmonic signal demodulation. The details
 of the model are presented in the methods section and in refs
 26, 28, 30, and 31. The n^{th} harmonic of the electric field
 component of the scattered light is written as $E_n = S_n e^{i\varphi_n} \propto (1 +$
 $r_p)^2 \alpha_{\text{eff}}(\beta) E_{\text{inc}}$ where r_p is the far-field Fresnel reflection
 coefficient of the sample,²⁹ the incident electric field, and
 $\alpha_{\text{eff}}(\beta)$, the effective polarizability,³⁰ which contains the near-
 field interaction between tip and sample. The quasi-static near-
 field reflection coefficient, β , is a function of the frequency-
 dependent dielectric function, $\epsilon(\omega)$, of the sample (see
Methods for the equation for β with a multilayer model). It
 is clear from **Figure 2c,d** that only when the out-of-plane axis
 dielectric data are used in the calculation that we reproduce the
 experimental near-field nano-FTIR amplitude and phase
 spectra. The experimental spectra shown in blue solid lines,
 amplitude (**Figure 2c**) and phase (**Figure 2d**), fit reasonably
 well with the extended finite dipole model calculations that
 uses the out-of-plane dielectric data as shown in black solid
 lines. The model calculations performed using the in-plane
 dielectric function (red solid lines in **Figure 3c,d**) significantly
 deviate from the experimental spectra. This is because light
 focused on the metalized tip is mainly enhanced along the tip-
 axis, perpendicular to the sample surface, and probes the
 sample largely in the out-of-plane direction, which is then
 scattered by the tip and detected. The small deviation of the
 theoretical phase spectra from the experiment (**Figure 2d**) may
 be due to the tip probing both components (in-plane and out-
 of-plane) in some proportion instead of exclusively the out-of-
 plane component, as assumed in the calculation.

In **Figure 3a** we show representative images of topography
 and monochromatic s-SNOM amplitude (b, d, and f) and
 corresponding phase (c, e, and g) images of muscovite mica
 exfoliated on a Si substrate taken at three selected excitation
 laser frequencies (1030 , 1075 , and 1175 cm^{-1}). Additional
 monochromatic images at several other excitation frequencies
 are shown in **Figure S3**. The excitation frequency of 1075 cm^{-1}

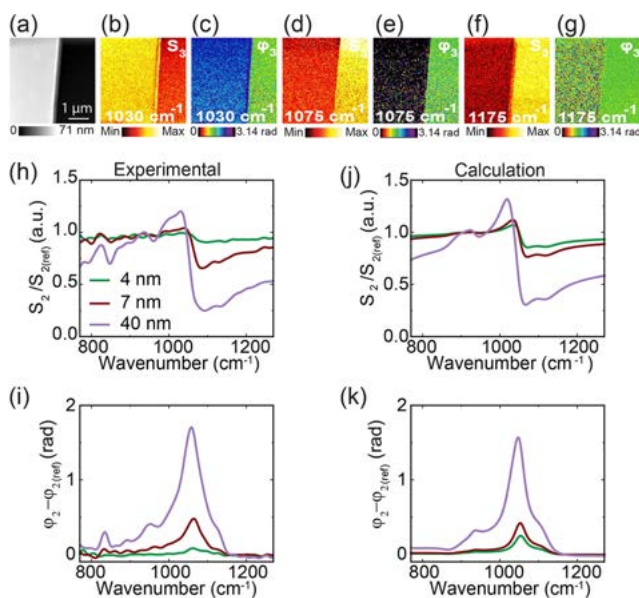


Figure 3. s-SNOM images and nano-FTIR of mica on Si substrate. (a–g) Topography, third harmonic near-field amplitude, and phase images at three different frequencies of 55 nm mica flake on Si. Near-field experimental nano-FTIR amplitude S_2 (h) and phase φ_2 (i) spectra at different thicknesses. Calculated nano-FTIR amplitude S_2 (j) and phase φ_2 (k) spectra.

is of particular interest since it is in the hyperbolic polaritonic range (1050–1130 cm^{-1}) of mica. However, the amplitude/phase images do not display the characteristic interference fringes that are the hallmark of polaritonic propagating modes. We attribute this lack of propagating modes to large losses.³² The amplitude contrast between mica and Si is inverted at 1030 cm^{-1} due to the large negative $\text{Re}(\epsilon_1)$ that enables the normalized amplitude of mica to be larger than unity, whereas wavenumber at 1030 cm^{-1} and larger give mica amplitude contrasts smaller than unity resulting darker profiles than the surrounding Si. To understand the full wavelength and thickness dependent IR optical characteristics, we took nano-FTIR spectra on varying thickness flakes of muscovite mica (thickness \sim 4, 7, and 40 nm) on a Si substrate. Silicon is a choice substrate for this purpose, since its spectra is featureless in the mid-IR spectral region. In Figure 3h,i we show the experimental normalized amplitude and phase spectra, respectively. Experimentally, these spectra were obtained by normalizing the broadband spectra taken on the mica flake to spectra collected from a reference point on the Si substrate surface.^{26,27} The calculation results shown in Figure 3j,k were performed using the extended finite dipole model calculation in which the out-of-plane dielectric function of mica extracted from ellipsometry measurements (as described above) were used to achieve the near-field amplitude and phase spectra of varying thicknesses of muscovite mica exfoliated on Si substrate in the frequency range 750–1300 cm^{-1} . Both the experimental amplitude and phase spectra show similar appearances for different layer thicknesses; however, the signal level becomes progressively smaller with decreasing thickness due to a smaller probed volume. The phase spectra show a prominent broad peak around \sim 1080 cm^{-1} . The calculations reproduce the essential features of the experimental amplitude and phase spectra in peak positions and displays thickness dependence signal intensity similar to experimental observa-

tions. The broad, strong band between 980 and 1200 cm^{-1} centered around \sim 1080 cm^{-1} is due to stretching vibrations of Si–O, which is in better agreement with several reported data.^{33–35} The shoulder at 831 cm^{-1} is due to the stretching Al–O mode, whereas the band near 920 cm^{-1} is tentatively assigned as a mixed modes arising from Al–OH stretch, Al–O–Al vibration, and Si–O–Si and Si–O–Al stretching vibrational modes.^{33–37}

We took infrared nano-FTIR spectra of heterostructures of various thicknesses of muscovite mica exfoliated on SiO_2 . We chose SiO_2 as a supporting substrate because of its strong phonon resonance absorption peak that partially overlaps with mica that may enable phonon–polariton-enhanced IR spectroscopy. In addition, unlike Si, SiO_2 substrate enables facile exfoliation of thin layers of mica down to a monolayer. To investigate the property of hyperbolic modes in mica exfoliated on SiO_2 , we took topography (Figure 4a) and near-field

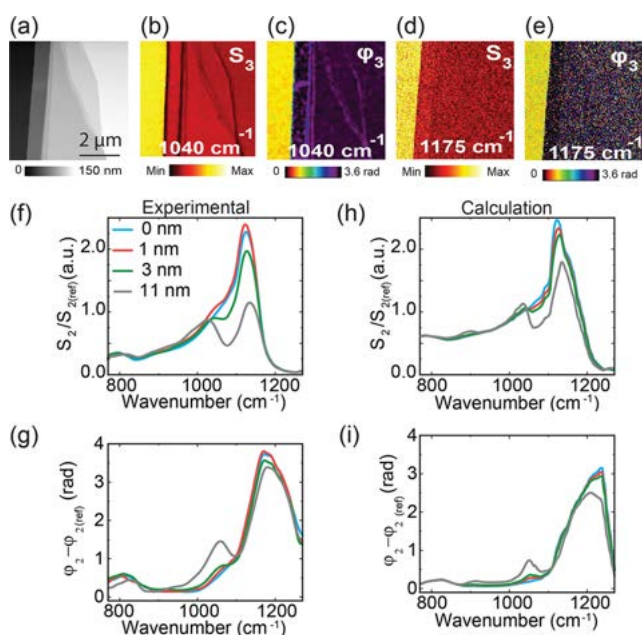


Figure 4. s-SNOM images and nano-FTIR of mica on SiO_2 substrate. (a) Topography image of the mica flake. (c–e) Third harmonic near-field amplitude and phase images of the flake in (a) at two different frequencies. Near-field experimental nano-FTIR amplitude S_2 (f) and phase φ_2 (g) spectra at different thicknesses. Calculated nano-FTIR amplitude S_2 (h) and phase φ_2 (i) spectra.

amplitude (Figure 4b,d) and the corresponding phase (Figure 4c,e) images at two excitation laser frequencies (1040 and 1175 cm^{-1}). We did not observe propagating modes; however, we observed an enhanced polaritonic signature in the near-field images taken at the hyperbolic spectral range (\sim 920–1130 cm^{-1}). For example, as shown in Figure 4b, the amplitude and phase images taken at 1040 cm^{-1} show enhanced signal at the topographic steps at different heights, whereas such signatures are lost at 1175 cm^{-1} , which is outside the hyperbolic range (see Figure S4 for more monochromatic images at other excitation frequencies). Similar to the discussion following Figure 3, the absence of clear propagating modes here is also attributed to the weak polaritonic behavior of mica and large losses. In Figure 4f,g we show the experimental amplitude and phase spectra of exfoliated mica down to a monolayer on SiO_2 substrate taken in the IR range (750–1280 cm^{-1}). The

heterostructure spectra intensity significantly depends on the thickness of the mica layer. As the thickness of the mica decreases, the signal level for all the spectra features arising from the top mica layer (discussed above) progressively decreases, while the known broad peak of SiO₂ centered around ~1180 cm⁻¹ in the phase spectra increases in intensity. We observe a spectral signature of a monolayer thickness. This is evident when comparing the blue and red curves in Figure 4g; the weak shoulder at 1080 cm⁻¹ is a clear indication of absorption coming from ~1 nm thick mica (see Figure S5, zoomed in plots of the phase spectra for 0, 1, and 3 nm for better comparison). This is because of substrate-enhanced absorption due to the combined polaritonic behavior of both mica and SiO₂ in these IR frequency ranges. Furthermore, for a mica flake as thick as 310 nm, we see through it a signature of the SiO₂ spectral signature (see Figure S6), possibly due to the polaritonic behavior of both mica and SiO₂. These experimental trends are reproduced faithfully in intensity changes with thickness and peak positions by the extended finite dipole model calculations (Figure 4h,i) performed using the dielectric function of muscovite mica (as described above) and of SiO₂ from literature.³⁸

CONCLUSION

We investigated the infrared optical properties of the muscovite monolayer to multilayer mica by a combination of ellipsometry and s-SNOM/nano-FTIR experimental measurements and analytical calculations based on the extended finite dipole method. The dielectric function of muscovite mica in the mid-IR frequencies was extracted from ellipsometry measurements along the in-plane and out-of-plane axes (with respect to the sample plane). These measurements show that mica is a hyperbolic material having the in-plane and out-of-plane components of its dielectric permittivity opposite signs in the IR frequency range 920–1130 cm⁻¹, displaying weak Type I and Type II hyperbolic behavior. Near-field nano-imaging experiments did not find interference fringes of propagating modes expected from polaritonic medium, which may be due to the weak polaritonic behavior of mica and large losses. The extended finite dipole model calculations reproduce the essential features of the experimental amplitude and phase spectra in peak positions and thickness dependence signal intensity when the out-of-plane axis dielectric data is used in the calculations. The prominent broad peak in the phase spectra centered around ~1080 cm⁻¹ is assigned to stretching vibrations of Si–O, and the shoulder peak at 831 cm⁻¹ is due to the stretching Al–O mode; the band near 920 cm⁻¹ is tentatively assigned as a mixed mode arising from the Al–OH stretch and Al–O–Al, Si–O–Si, and Si–O–Al stretching vibrational modes.

METHODS

Extended Finite Dipole Model For Layered Systems.

The theoretical approach is based on the finite dipole model and its extension to the layered system in which amplitude (S_n) and phase (φ_n) are calculated by scattered emission:

$$E_n = S_n e^{i\varphi_n} \propto (1 + r_p)^2 \alpha_{\text{eff}} E_{\text{inc}} \quad (1)$$

In eq 1, for mica flake on SiO₂ on Si, r_p is the reflection coefficient for four layers (layer 1 is the surrounding medium, layer 2 is mica with a thickness d_1 , layer 3 is SiO₂ with a thickness d_2 , and layer 4 is Si) that can be calculated from a

multilayer Fresnel reflection coefficient for p-polarized light given by^{39,40}

$$r_p(q, \omega) = \frac{r_{12} + r_a \exp(2ik_z(d_1 + d_2))}{1 + r_b \exp(2ik_z(d_1 + d_2))} \quad (2)$$

where r_a and r_b can be calculated as

$$r_a = r_{12}r_{23}r_{34} \exp(-2ik_z d_1) + r_{23} \exp(-2ik_z d_2) + r_{34} \quad (3)$$

$$r_b = r_{23}r_{34} \exp(-2ik_z d_1) + r_{12}r_{23} \exp(-2ik_z d_2) + r_{12}r_{34} \quad (4)$$

r_{ij} is a single interface Fresnel reflection coefficient:⁴⁰

$$r_{ij} = \frac{\epsilon_j k_{z,i} - \epsilon_i k_{z,j}}{\epsilon_j k_{z,i} + \epsilon_i k_{z,j}} \quad (5)$$

where $k_{z,i} = \sqrt{\epsilon_i(\omega/c)^2 - q^2}$.⁴¹ In eq 1, α_{eff} is the effective polarizability. Equations 6–15 give us the effective polarizability, which is described in ref 30. L is the effective length of the tip, R_t is the tip curvature radius, which is 20 nm, C is the height-independent constant with $Q_0 = R_t^2 E_0$, which is the total amount of the polarization charge induced in the tip in the absence of sample, which is described in ref 28, and H is the tip and sample distance.

$$\alpha_{\text{eff}} = C \left(1 + \frac{f_0(H)\beta(\epsilon)}{2(1 - f(H)\beta(\epsilon))} \right) \quad (6)$$

$$f_0(H) = \left(g - \frac{2H + W_0 + R_t}{2L} \right) \frac{\ln \frac{4L}{4H + 2W_0 + R_t}}{\ln \frac{4L}{R_t}} \quad (7)$$

$$f(H) = \left(g - \frac{2H + W_i + R_t}{2L} \right) \frac{\ln \frac{4L}{4H + 2R_t}}{\ln \frac{4L}{R_t}} \quad (8)$$

$$C = L \frac{Q_0}{|E_0|} \quad (9)$$

$$W_0 \approx 1.31R_t L / (L + 2R_t) \quad (10)$$

$$W_i \approx R_t / 2 \quad (11)$$

β is the quasi-static, near-field reflection coefficient given by³⁹

$$\beta = \frac{\beta_{12} + \beta_a \exp(-2q(d_1 + d_2))}{1 + \beta_b \exp(-2q(d_1 + d_2))} \quad (12)$$

where β_a and β_b can be defined as

$$\beta_a = \beta_{12}\beta_{23}\beta_{34} \exp(2qd_1) + \beta_{23} \exp(2qd_2) + \beta_{34} \quad (13)$$

$$\beta_b = \beta_{23}\beta_{34} \exp(2qd_1) + \beta_{12}\beta_{23} \exp(2qd_2) + \beta_{12}\beta_{34} \quad (14)$$

The electrostatic reflection coefficient β_{ij} is defined by³⁹

$$\beta_{ij} = \frac{\epsilon_j - \epsilon_i}{\epsilon_j + \epsilon_i} \quad (15)$$

For further comparisons and details on the finite dipole model and the extended finite dipole model for layered systems, see the SI.

383 ■ ASSOCIATED CONTENT

384 ■ Supporting Information

385 The Supporting Information is available free of charge at
386 <https://pubs.acs.org/doi/10.1021/acsp Photonics.0c00951>.

387 Permittivity for different in-plane axes, near-field images
388 of mica/Si, near-field images of mica/SiO₂, zoomed in
389 nano-FTIR spectra of different thicknesses of mica, and
390 nano-FTIR amplitude and phase thickness of mica
391 (PDF)

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