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Scaffolding for nanotechnology: extraordinary infrared transmission of metal microarrays for stacked sensors and surface spectroscopy

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Abstract

Self-assembled monolayers, phospholipid bilayers, and membrane bound proteins are assembled on a subwavelength metallic array. These assemblies are assayed with direct infrared absorption spectroscopy which is greatly enhanced due to the extraordinary infrared transmission of the arrays. Stacking the arrays, one upon another, accentuates the surface plasmon properties and provides the basis of a nanospaced capacitive sensor.

1. Introduction

Periodic subwavelength arrays (both microscale [1] and nanoscale [2]) have been found to transmit more light than is incident upon their holes, i.e. they exhibit Ebbesen's extraordinary transmission effect. In simple terms, light initially incident upon metal excites surface plasmons (SPs) that propagate along the surface until they come to a hole. The SPs can tunnel through the hole, reemerging as photons on the other side of the metallic membrane, without being scattered out of the incident beam. We have pushed Ebbesen's extraordinary transmission effect [2] into the infrared (IR) spectral region using metallic microarrays enabling a new way to excite SPs on the arrays simply by placing them in a traditional, bench-top FTIR spectrometer [1]. The SPs facilitate unexpectedly large resonant transmissions throughout the IR spectral region which match the fundamental range of molecular vibrations. While our initial work [1] focused on lifetimes and dispersion of SP-mediated transmission resonances, this paper focuses on preliminary applications.

Microarrays can be thought of as the scaffolding of nanotechnology. They provide an interface between the macroworld and nanoworld since a microchannel can be located macroscopically with optical microscopes.

Microarrays present a means of organizing, locating, and studying individual nanotechnological constructions within microchannels. We present a sequence of increasingly complex nanoassembly procedures within the microchannels as assayed with absorption spectroscopy enabled by the extraordinary IR transmission of metal microarrays. It starts with application of self-assembled monolayers to the microchannels, proceeds to the addition of lipid bilayers, and ends with the incorporation of a nanochannel-containing protein within the layers. These metallic arrays are stacked, one upon another, to enhance the SP properties and provide the basis of a nanospaced capacitive sensor. In the long run, these devices could serve as the sensors in combinatorial and arrayed techniques for the rapid, sensitive, and molecule-specific optical or IR detection of nanotechnological constructions, DNA, and membrane bound species. The techniques and sensors developed in this work could also be applied to bioagents and chemical toxins which are currently of great national interest.

In 1998, Ebbesen and co-workers [2] reported the fabrication of square arrays of holes in silver films (150 nm hole diameters, 900 nm hole-to-hole spacing, 200 nm thickness) that produced unexpectedly large resonant transmissions in the visible and near IR regions. The films were optically



Figure 1. An SEM image of a Buckbee-Mears Ni mesh is inset showing an open area of 26%. The zero-order FTIR transmission spectrum at perpendicular incidence ($\theta = 0$) shows a maximum of 77% at ~700 cm⁻¹, i.e. Ebbesen's extraordinary transmission effect. The peaks are labelled by the *i*, *j* indices of equation (1).

thick and only transmitted by virtue of the perforations. The primary resonance occurred at a wavelength nearly ten times the diameter of an individual hole, while the transmission was twice the fraction of open hole surface area and a thousand times greater than the transmission expected for isolated holes. Ebbesen and co-workers attributed this behaviour [2–5] to the excitation of SPs by incident light and the details are still being elucidated [5, 6].

SPs are electromagnetic excitations of the metal's conducting electrons at the surface of the metal. A grating, prism, or subwavelength feature is needed to couple light and SPs as they cannot be directly excited by light [15]. They are important in advanced immunosensors and biosensors [7], in situ binding of DNA [8, 9] without labelling, detection of protein binding in lipid bilayers [10, 11], optoelectronic devices, wavelength based assay and imaging [8], prism based ATR [12] such as in the Biacore commercial instrument, plasma waveguide ATR (Aviv commercial instrument), nonlinear optics [13], and near field microscopy [14]. When the enhanced surface electric fields of SPs [15] and the possibility of resonant multipassing effects [5] are considered, there is great scientific and technological potential in the application of metallic subwavelength hole arrays. This work opens a new way to access SPs. While other techniques for accessing SPs exist (such as ATR [14, 16]), the present technique does not require lasers, prisms, or angle tuning. The metallic array is simply placed in a traditional, bench-top FTIR spectrometer and a transmission spectrum is recorded.

2. Extraordinary transmission of nickel mesh in the IR

Very fine, biperiodic, metallic mesh is available from Buckbee-Mears (278 East 17th St., St Paul, MN 55101). It is only available in nickel and has square holes of 6.5 μ m width, a square lattice hole-to-hole spacing of 12.7 μ m, and a thickness of 5 μ m. The complex dielectric constant of nickel [17] is not useful for SPs in the visible regime (unlike for gold and silver); however, it becomes favourable below ~3000 cm⁻¹.



Figure 2. The IR photonic energy band diagram of a Ni microarray in the Γ X and Γ M directions (defined in the inset for a square lattice in reciprocal space). Filled circles are peak positions and open circles are shoulders (by second derivatives).



Figure 3. An FTIR transmission spectrum of Buckbee-Mears Ni mesh with holes closed down to 3 μ m. The resonances narrow as compared to figure 1. The labels (*i*, *j*) show the locations of resonances as predicted by equation (1). The resonances broaden with increasing wavenumber and are extensively overlapped.

At perpendicular incidence, a square metallic array will have transmission resonances approximately given by [3, 15]

$$\tilde{\nu}_{\max} = \frac{\sqrt{(i^2 + j^2)}}{Ln'_{\text{eff}}} \tag{1}$$

where *L* is the lattice spacing, *i* and *j* are integer steps along the reciprocal lattice vectors (like diffraction spots), and n_{eff} is the real part of the effective index of refraction. A zero-order FTIR transmission spectrum of the Buckbee-Mears nickel mesh (figure 1) was recorded with mesh perpendicular to the spectrometer's beam [1]. The mesh transmits 77% of the light even though only 26% of the mesh is open area!

The SP nature of the extraordinary transmission is investigated by following the positions of resonant transmissions versus angle (θ) of the mesh relative to the incident beam [1]. An IR photonic energy band diagram is constructed from such data, as shown in figure 2. The resonant positions ($\tilde{\nu}$) of the square lattice are plotted against the



Figure 4. SEM images of Cu deposited on Ni mesh in a sequence of longer deposition times producing 6, 5, 3, and 2 μ m aperture widths (from top left to bottom right) of surprising uniformity.



Figure 5. FTIR transmission spectra of a Buckbee-Mears Ni mesh $(L = 12.7 \ \mu\text{m})$ that was coated with copper until the holes were $\sim 3 \ \mu\text{m}$ wide (dotted, upper trace) and upon additional coating with a SAM of 1-dodecanethiol (solid, black trace).

dispersion, $2\pi \sin(\theta)$, in the ΓX direction (i, j = 1, 0) [1] on the right side of figure 2, and in the ΓM direction (i, j = 1, 1)on the left side. To take ΓX data, the mesh lattice was aligned with the spectrometer's vertical polarized E-field, such that rotation about this axis investigated transverse magnetic (TM) polarization. To take ΓM data, the mesh axes were rotated to a 45° angle with respect to the spectrometer's vertical polarized E-field. The primary resonance at 700 cm⁻¹ and $\theta = 0$ (perpendicular incidence) would be fourfold degenerate by equation (1); however, this degeneracy is lifted in practice. The primary resonance at $\theta = 0$ breaks into three sets of resonances. The limiting slopes of these sets of resonances can be derived and roughly predicted by the theory of SPs on infinite air/metal interfaces [1, 15]. Understanding these details is a problem at the forefront of optical physics. We believe that these are the first measurements of the dispersion of the extraordinary transmission of metallic microarrays in the ΓM direction of a square lattice providing further compelling evidence for SPs. These resonances show large band gaps (~11% of resonance energy at zero dispersion) that are complicated by the lifting of equation (1) degeneracy. The intrinsic widths of SP resonances suggest significant narrowing upon moving into the IR, and considerable narrowing is observed. The intrinsic limitation, 'internal damping', is the creation of 'electron-hole pairs at the Fermi level' by the field of the SP [15]. Our current meshes are a factor of ~ 100 away from this intrinsic limitation, so there is still much room for narrowing of the resonances. In practice, a number of other factors contribute to the width of the resonances including the thickness of the film, roughness of the surface, uniformity of the array, and width of the holes. The isolation of a single resonance at low wavenumbers by angle tuning has allowed the resonant lineshape to be more rigorously investigated [1]. Lineshapes revealed lifetimes that vary over a range of 100-500 fs which is considerably longer than the lifetimes observed in the visible region (7 fs) [18]. SPs travelling near the speed of light can propagate hundreds of microns along the surface within such intervals. Propagation over such distances provides an opportunity for long absorption path lengths which we believe to be the most important factor in the 1000-fold enhancements observed for IR absorption by surface species.

3. Effect of hole size—Cu deposition

The size of the holes can have a dramatic effect on the transmission resonances of a metallic microarray. Although the Buckbee-Mears Ni mesh comes with high regularity, the holes get smaller at the outer edge of the sheets. The resonances in figure 3 from mesh with 3 μ m holes are narrower than in figure 1 (6.5 μ m holes) and resonances of higher *i*, *j*



Figure 6. Enhanced IR absorption spectra of alkanethiol SAMs on Cu-deposited mesh showing Snyder CH_2 wagging progressions: 1-dodecanethiol (bottom, C_{12}), 1-tetradecanethiol (middle, C_{14}), and 1-hexadecanethiol (top, C_{16}).

values are more in evidence. The transmission range of these meshes matches the traditional range of fundamental molecular vibrations enabling vibrational spectroscopy.

We invented a method to uniformly close down the hole widths by electrochemical deposition of copper. Reduction of the hole widths with copper: (1) narrows the resonances and increases the lifetimes of the SPs, and (2) allows the application of alkanethiol self-assembled monolayers which are not stable on nickel oxide [19]. The starting point for all of the meshes used in this work is the Ni 2000 line in⁻¹ electroformed micromesh from Buckbee-Mears, Inc. This mesh is created from a mask using UV lithography, so the holes are located within 1 μ m over the whole 6" \times 6" sheet. This creates great regularity and high tolerances in the geometry of the holes. The walls of the holes are not perfectly perpendicular to the surface. Angles of 6° -10° to the surface normal produce a tapering of nominally 8 μ m holes to 6.5 μ m across the thickness. The mesh is created on a very flat mandrel producing variations in the nominally 5 μ m thickness of 200 nm over the whole $6'' \times 6''$ sheet and a few nanometres in local regions. A roughly $5 \times 5 \text{ mm}^2$ piece of Ni mesh (Buckbee-Mears 2000 lines in⁻¹, electroformed) is spaced by $\sim 2 \text{ mm}$ from a ring-shaped Cu electrode in an aqueous solution of 1.5 mol% CuSO₄. The application of an over-voltage of -10 V to the base nickel mesh drives a 10 s spike of deposition current (maximum of ~ 0.2 A) producing an unexpectedly uniform coating. Further deposition proceeds at less than $\frac{1}{5}$ of the peak current resulting in further closing of the holes and growth of Cu crystallites. The final widths of the holes can be varied from 6.5 to $<1 \,\mu$ m by varying the deposition time as shown in figure 4. A run of 90 s produced $\sim 2.4 \ \mu m$ holes in these trials. Hole widths were measured with scanning electron microscopy (SEM) and optical microscopy. Statistics gathered over ten different holes in each of ten different regions reveal an estimated standard deviation of $\sim 0.2 \ \mu m$. The resulting meshes are rugged and easy to handle. They can be heated and coated, and they are amenable to additional processing to make nanosize holes or nanoassembly within. Details on the effect of hole width on the zero-order transmission

spectra will be reported elsewhere [20]. In general, the resonances get narrower with decreasing hole width, until they are no longer detectable at the smallest hole widths. This reveals a transition from SP dominated behaviour to waveguide dominated behaviour. The wavenumber threshold for transmission in a square waveguide [21] is nominally $\frac{1}{2a}$ where *a* is the square hole width. An aperture width of ~ 3 or 4 μ m provides a good compromise between resonance narrowness and transmission over the whole fundamental range of vibrations.

4. Preliminary applications of the extraordinary transmission effect

The following subsections illustrate some initial discoveries that are being developed into applications. They demonstrate the feasibility of applications of the extraordinary IR transmission effect.

4.1. High quality IR absorption spectra of alkanethiol monolayers

Strategies to build more complex assemblies within microchannels might start with a self-assembled monolayer (SAM) coatings. There are a number of published recipes for alkanethiol (CH₃(CH₂)_nSH) SAMs on copper [22-24]. Figure 5 displays IR transmission spectra of a Cu-deposited mesh before (dotted trace) and after (solid trace) dipping in 20 mM 1-dodecanethiolate in toluene for 30 min to create a SAM (hydrocarbon chain of 12 C atoms bound to the surface by a S atom). We observe a shifting of the resonances (and slight reduction of transmission) upon coating, which is the wavelength equivalent of ATR experiments. More importantly however, we also observe molecular absorptions (circled in figure 5) of the monolayer coatings that can be converted into absorption spectra. Points are chosen along the transmission curve excluding the molecular absorptions and a spline fit is accomplished to provide a background. Absorption spectra are

presented as $-\log(\text{sample/spline background})$. We dipped Cu-deposited mesh in several different 20 mM alkanethiol (12, 14, and 16 C atoms in length) solutions in toluene [25] overnight. After drying and waiting a day for crystallization, the transmission spectra were recorded and converted to absorption spectra as shown in figure 6 (1 cm^{-1} resolution, 1000 scans each). These are the highest quality direct IR absorption spectra for such monolayers (covering the full vibrational range) of which we are aware. There is a great deal of IR work on alkanethiols to guide the interpretation of these spectra [23, 26-30] with most work in the C-H stretch region. A definitive paper by Whitesides and co-workers [23] says 'The low frequency modes, while rich in information, are sufficiently weak in intensity as to preclude quantitative analysis'. The expanded region (inset in figure 6) shows Snyder's CH₂ wagging progression [31–33] which corresponds to alltrans chain configurations and testifies to an enhanced ability to work in the low frequency regions. These progressions are related to those seen in n-paraffins as analysed by Snyder and co-workers [31, 33, 34, 51], in n-alkanoic acid monolayers [29], and as seen in related multilayer systems [35]. The progression frequencies exhibit monotonic trends versus $\frac{k}{N+1}$ (k = 1, 2, 3, ..., N is the transition index, N is the number of CH_2 groups in the chain). The trend is linear at low k, then transition spacings reduce, and transitions converge to the value of the infinite methylene chain (polyethylene). We are aware of only one other study [29] that has seen the Snyder wag progression in a monolayer (n-alkanoic acids). Octadecanethiol SAMs on Cu have been assayed with reflection absorption infrared spectroscopy (RAIRS) exhibiting 0.002 au absorptions by Whitesides and co-workers [23], 0.0005 au by Ron et al [25], and 0.001 au by Laibinis and co-workers [24] in the C-H stretch region at high angles. We observe absorbances of ~ 0.2 which are more than 100 times greater than literature reports. Direct IR absorption using the extraordinary IR transmission effect presents a new opportunity to learn molecule-specific details about binding to membranes. Contrast this with ATR where a generic change in the membrane's dielectric constant indicates binding, i.e. molecules rather than spectroscopy provide specificity. The wagging progression transitions shown in figure 6 have FWHM that are $<3 \text{ cm}^{-1}$ even though they were recorded at room temperature. Better spectra enable more incisive normal mode analyses and better diagnostics for membrane structure.

4.2. Phospholipid bilayers

Once an alkanethiol SAM has been applied to a Cu-deposited mesh, then more complex self-assembled layers can be applied, such as phospholipids, to establish a supported lipid bilayer membrane (s-BLM) [10, 28, 32, 36, 38–40]. The IR transmission spectrum of a bare Cu-deposited mesh (top, black trace) is shown in figure 7. The mesh was coated with hexadecanethiol SAM (middle, grey trace), and then dipped (several times for a few seconds) in dipalmitoyl phosphatidylcholine (DPPC, the most common phospholipid in cells) solution in CCl_2H_2 (bottom, light grey trace). The successive coatings cause shifts in the positions of the transmission resonances (analogous to ATR experiments) and molecular absorptions become evident (circled in figure 7).



Figure 7. Transmission spectra of a Buckbee-Mears Ni mesh $(L = 12.7 \ \mu\text{m})$ that was coated with copper until the holes were $\sim 3 \ \mu\text{m}$ wide (top trace). This mesh was coated with a hexadecanethiol SAM (middle) and then further coated with a DPPC phospholipid bilayer (bottom).



Figure 8. Absorption spectra of hexadecanethiol SAM on Cu-deposited mesh (black) and a further coating of DPPC phospholipid bilayer (grey).

Guided by the shape of the bare mesh spectrum, many points are chosen on both sides of the absorption features and fit with a spline function to define a background, and then the observed trace is analysed as $-\log(\text{sample/background})$ to obtain the absorption spectra shown in figure 8 (350 scans at 4 cm^{-1} resolution). Again, the absorptions are quite enhanced. The carbons chains of DPPC are the same length (16 C atoms) as in hexadecanethiol, so the threefold increase in the intensity of the C-H stretch region is taken as an indication that the DPPC has formed a bilayer (with a hydrophobic outer surface as determined by the contact angle of water drops). Phospholipid bilayers undergo a transition from a gel phase (very crystalline and ordered) to a liquid crystal phase (very fluid) at temperatures that vary with the degree of hydration. These spectra track molecular geometry details and phase of these membranes. In the C-H stretching region there are well-known strategies [30] for analysis of the relative intensities for the inclination and twist angles of the methylene chains, as well as peak positions for the phases [37] of such systems. Since Snyder wagging progressions can be observed on top of the prominent phosphate vibration in ours and other



Figure 9. The IR transmission of a 4-stack of Buckbee-Mears Ni mesh emphasizes the SP transmission and suppresses non-metallic transmission.

work [32, 40, 52], it will be interesting to see how these compare to alkanethiol monolayers and *n*-paraffins.

4.3. Stacking—preliminary studies for a new sensor

If two pieces of Buckbee-Mears Ni mesh are stacked in contact, one upon the other, the stack still exhibits the extraordinary transmission effect. In previously reported work [1], two Buckbee-Mears Ni meshes were stacked giving transmittance of six times the fractional open area! The spectra versus incident angle showed the same SP-mediated dispersion as a single mesh. In fact, the SP-mediated transmission seems to be accentuated relative to the non-metallic transmission (which probably suffers from the lack of alignment between the two meshes). The IR transmission spectrum of a stack of four Ni meshes in contact is shown in figure 9. We estimate that the 4-stack has 0.5% open area, so the 22% transmission exhibited in figure 9 reinforces the idea that the light primarily travels along the surface, not through the middle of the holes. A single Ni mesh (transmission of 84% at 690 cm⁻¹) was coated with a dodecanethiol monolayer (30 mM dodecanethiol/ethanol) resulting in the IR absorption spectrum (bottom trace) shown in figure 10. This spectrum is again greatly enhanced; however, it decays in \sim 30 min as alkanethiols can be unstable on oxidized Ni surface [19, 41]. After seeing the benefits of stacking uncoated mesh with regard to the SP-mediated transmission resonances, we became curious as to the ability of self-assembled monolayers to control or affect the stacking process. In principle, the coatings could prevent direct contact between metallic meshes in the stack by virtue of the lipid bilayer of several-nanometre spacing produced upon stacking. By analogy to the self-assembly of cell-like, lipid bilayer membranes, we suspected that if two alkanethiolate-coated meshes, freshly removed from ethanolic solutions, were laid one on top of the other, then the polar solvent would be excluded as the hydrocarbon chain ends found more favourable intermolecular interactions with similar hydrocarbon chain ends from the other mesh coating. In practice it took a number of dippings of Ni mesh in 30 mM dodecanethiol/ethanol solution before strong IR spectra of the alkanethiolate were observed. Once these signals were observed, the meshes were dipped again and then stacked



Figure 10. IR absorption spectra in the C–H stretching region of a single Ni mesh coated with dodecanethiol and two Ni meshes coated with dodecanethiol and stacked producing a lipid bilayer spacing which glues the two meshes together (top trace).

before the solvent could evaporate. The meshes stick together when prepared in this way (unlike bare, uncoated meshes). The flatness of the original mesh and the fact that the alkanethiolcoated meshes stick to each other suggest the possibility of extensive regions with a capacitive spacing of several nanometres as determined by the length of the alkanethiols. The IR absorption of the 2-stack is five times greater (not twice as great) as shown by the top trace in figure 10, and the signal lasted for a day (rather than the 30 min for a single piece of Ni mesh, due to reduced access in the bilayers to O₂(g) and surface cleaning associated with the H(ads) created upon successive alkanethiolate coatings). Stacking provides a nonlinear increase in surface absorption which suggests that light (in the form of SPs) moves between the two separate meshes where there is enhanced opportunity for absorption by the bilayer. Work is currently under way to measure the macroscopic capacitive properties of this arrangement. Capacitance is directly related to the spacing, area, and dielectric constant of the spacer (~ 2.16 for hydrocarbons [24]). Noting that phospholipid bilayers have capacitance [42] of \sim 400 nF cm⁻² as measured with 25 mV, 5 kHz Wheatstone Bridge excitations, such measurements should be feasible and informative. If nanospaced capacitors can be produced in this self-assembled manner, then a new type of sensor is obtained where voltages can be applied or extracted from the stack of meshes. Electric fields could be applied to contents of the lipid bilayer. We imagine choosing the lattice parameter of the mesh stack to match the most intense vibration of a target molecule and stacking as many meshes as necessary to get the path length needed to obtain large fractional absorptions.

4.4. Trapping the membrane bound protein, gramicidin, in mesh stacks

A vast amount of biochemistry becomes available for study by imbedding protein in the lipid bilayer of a mesh stack. Gramicidin [43, 44] (see figure 11) has been chosen for study as it is: a prototypical membrane bound protein, a well-known antibiotic, small enough for performing vibrational analysis on a powerful desktop PC, and a nanochannel building block on the road to complex nanoassembly within microchannels.



Figure 11. PM3 optimized gramicidin A monomer (membrane structure). 15 amino acids, alternating L and D, coil into a nanochannel. A single-stranded, helical dimer (HD) spans a membrane allowing ion transport. O atoms (dark) of C=O groups line the ion channel.



Figure 12. Transmission spectra of two meshes lightly coated with copper before (dotted traces) and after (upper solid traces) coating with a hexadecanethiolate monolayer. A drop of gramicidin D solution was applied to one of the meshes and then they were stacked, producing the transmission spectrum of the lower plot.

Transmission spectra are shown in figure 12 for two meshes with light copper deposits (hole size of 5.6 and 5.5 μ m for meshes 1 and 2, respectively, as shown with dotted curves in the top plot). Both meshes were coated with a SAM using a 20 mM hexadecanethiol/toluene solution yielding the solid traces shown in the top plot of figure 12. There is a significant red-shift in the transmission resonances (change in the effective index of refraction of the interface) and evidence of molecular absorptions. After these transmission spectra were recorded, the meshes were redipped overnight in 20 mM



Figure 13. IR absorption spectra of gramicidin D on a hexadecanethiolate-coated, two-mesh stack (solid trace) and a spectrum of the same stack recorded five months later (grey trace). The dotted traces show the absorption spectra of the hexadecanethiolate coatings of each mesh before they were stacked.

hexadecanethiol/toluene solution. Quickly, after the meshes were removed from solution, a drop of CH₂Cl₂ containing gramicidin D was applied to one of the meshes which rapidly spread over the whole mesh. The meshes were then laid one upon the other and they were observed to stick to each other. The interference pattern from an optical microscope image revealed that the meshes were rotated from each other by 2.1°. The IR transmission spectrum of the stack is shown in the bottom plot of figure 12. The maximal 35% and 25% transmissions of the individual alkanethiol-coated meshes were reduced to about 2% transmission upon stacking and the individual resonances appear more damped. Note that one could obtain a fractional open area of anything from 0-25% with this procedure. The stack's transmission spectrum reveals molecular absorptions that were converted to an absorption spectrum in figure 13. Also shown are absorption spectra of the hexadecanethiol SAMS of each individual mesh (dotted light grey) and an absorption spectrum of the stack recorded five months later (solid light grey trace). The meshes were still self-adhered after five months and the absorption spectrum was essentially unchanged. There are a number of features of this

preliminary experiment that need better control, such as surface roughness and amount of protein; but these results suggest that further studies would be worthwhile and work continues.

These results are particularly exciting to us because the molecular tools of physical chemistry are increasingly applicable to larger molecules. Since gramicidin is a small protein (only 276 atoms), we were able to use an experimental structure (the single-stranded helical dimer 1GRM structure from the Protein Data Bank, www.rcsb.org/pdb), optimize it (PM3 semi-empirical method as shown in figure 11) and obtain a normal mode analysis of all 822 vibrations. This will compliment existing normal mode analyses [45] with transition moments and enable comparison to the observed spectrum with regard to orientation. The most intense vibration is in the amide I band and consists of C=O stretches lining the nanochannel. Its position at 1633 cm⁻¹ indicates a helical structure [46]. With the addition of smoother metallic coatings, we will be in a position to investigate how such a spectrum changes with the protein's orientation relative to the metal surface. Our calculations indicate large components of dipole derivative both along and perpendicular to the channel. In fact the whole 'fingerprint' region will probably be very diagnostic. The shoulder to the high energy side of the amide I band region indicates the presence of more than one type of structure, which is well known from IR studies [43, 45, 47]. Crystallographic studies find double-stranded helices [48], while NMR studies in membranes find single-stranded, helical dimers [49]. There is IR work suggesting transformation between such structures with temperature [50]. It will be possible to calculate expected differences in the IR spectra of important structures and search for them versus temperature. Components of the dipole derivatives of all vibrations could be analysed with regard to possible orientations between the nanochannel and metal surface. Work is also under way to see how little protein is needed, i.e. how small a fraction of monolayer coverage is detectable.

5. Conclusions

A new way to access SPs has been developed simply by placing a subwavelength metallic array in a bench-top FTIR spectrometer. By moving into the IR, Ni has been added to the list of metals for SP work which is usually accomplished in the visible region using Au, Ag, and Cu. A broader range of metals, including Cr, Pt, Pd, and W should also be amenable to work in the IR. The long lifetimes of SPs in the IR create long absorption path lengths and >100-fold enhancements in the IR absorption of monolayers and surface species are observed. Enhanced direct IR absorption spectra have been recorded for alkanethiol monolayers, phospholipid bilayers, and a membrane bound protein. The high resolution and structure of these spectra promise to be powerful diagnostics for the geometry, phase, and structure of these assemblies.

Metallic subwavelength arrays have been stacked one upon another to enhance SP properties, reduce the nonmetallic transmission background (figure 9), increase surface absorption path length, and provide the basis for a nanospaced capacitive sensor in which the microarrays are spaced by alkanethiolate bilayers. The stacking of meshes represents a bench-top-accessible means with potential to create IR photonic crystals with self-assembled, controllable spacings (lipid bilayers) in the nanosize regime. This new type of SP-mediated transmission of single-mesh arrays is a forefront problem in optical physics [53]. Transmission band-pass behaviour of *single-mesh* arrays is a well-known phenomenon [54] in the microwave region: however, transmission greater than the fractional open area (extraordinary transmission) is new and deserving Stacking may allow the determination of investigation. dispersion and lifetimes of higher i, j resonances in a manner that has (so far) only been possible with the lower energy resonances for single-mesh arrays. Since current theory does not address important features such as damping lifetimes, lifting of the equation (1) degeneracies, and selection rules, basic experimental data are particularly important.

Preliminary work has been presented showing that mesh stacks enable the recording of enhanced IR absorption spectra of small quantities of the membrane bound protein, gramicidin. In addition to the obvious biochemical applications, some intriguing possibilities arise for nanotechnology. Since gramicidin allows passage of ions through a membrane, it may be possible to perform electrochemistry in the nanochannel using the meshes of a 2-stack as electrodes. It may be possible to deposit a nanoparticle or nanowire in the nanochannel with such assemblies.

The production, characterization, and initial applications of IR photonic membranes by means of square arrays of metallic, micron-sized apertures coated with alkanethiols, lipid bilayers, and embedded proteins have been demonstrated. As the world engages in the development of nanodevices, these new methods will enhance our ability to detect, probe, and image nanostructures at interfaces.

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