# Interaction of an infrared surface plasmon with an excited molecular vibration

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The interaction of an infrared surface plasmon and an excited molecular vibration was investigated by using a square array of subwavelength holes in a Ni film which supports propagating, surface-plasmon-mediated, transmission resonances. The largest transmission resonance [the  $(1,0)_{-}$ ] was tuned through the rocking vibration of the hexadecane molecule (at 721 cm<sup>-1</sup>) in a hexadecane film on the mesh by varying the thickness of the film. The interaction of the rocking vibration and surface plasmon is characterized spectroscopically by an increase in the intensity of the vibrational band by more than a factor of 2, variation of the vibrational line shape relative to the spectrum on a nonmetallic surface, and shifts in vibrational peak position by as much as 3.0 cm<sup>-1</sup>. Relationships are developed between the transmission resonance position and the thickness and dielectric properties of the coating. © 2007 American Institute of Physics. [DOI: 10.1063/1.2730781]

# INTRODUCTION

Freestanding Ni metal films with square arrays of subwavelength holes (meshes) have been shown<sup>1-6</sup> to exhibit Ebbesen's extraordinary transmission effect<sup>7</sup> in the infrared (IR), i.e., they have one or more resonances that transmit a higher fraction of incident light than the fraction of open surface area. There is clearly a role for propagating surface plasmons<sup>1,6,8</sup> (SPs) and a similarity of the dispersion to that of SPs on smooth air metal interfaces, such as those involved in metal-coated prisms and attenuated total reflection (SP-ATR) experiments.<sup>9,10</sup> The transmission resonances of freestanding mesh (even when excited at perpendicular incidence) exhibit behaviors analogous to SP-ATR experiments, including sensitivity to nanoscale changes in coating thickness $^{9,11}$  and the interaction of molecular electronic excited states and SPs (Refs. 9 and 12) in the visible. In these experiments, the primary transmission resonance is tuned both by the thickness of a coating and the incident angle of a spectrometer's beam in order to bring a molecular vibration into and out of resonance with an infrared SP-mediated transmission resonance.

## THICKNESS TUNING

When a Ni mesh [geometry given in Fig. 1(a)] is removed from neat hexadecane solution, some of the solvent spreads out over the mesh and a film of micron-scale thickness remains. The coating may remain for weeks due to the low vapor pressure of the 16-carbon-atom-long hydrocarbon. When the coated mesh is placed in a Fourier transform infrared (FTIR) spectrometer, the transmission spectrum is dramatically altered as shown in Fig. 1(b) (dotted trace is before coating and the solid trace is after coating). Notice that upon coating with hexadecane, there is a large redshift and broadening of the  $(1,0)_{-}$  resonance as well as dips associated with molecular absorptions. Absorption spectra are obtained from the trace using a smoothed background from a spline of points along the trace avoiding the molecular absorptions<sup>2-4</sup> [result shown in Fig. 1(c)]. A glow bar source heats the hexadecane film as the coated mesh sits in the FTIR and competition ensues between evaporation of the coating and heat



FIG. 1. (a) Scanning electron microscope images (SEMs) of freestanding Ni mesh. There is a rough (left) and a smooth (middle) side. The hole width is ~5  $\mu$ m, the square lattice spacing is 12.7  $\mu$ m, the film thickness is ~3  $\mu$ m (right image), and the percentage of the open surface area is 16%. (b) Zeroorder transmission spectra (Perkin Elmer spectrum GX, DTGS detector, 30 scans, 4 cm<sup>-1</sup> resolution) at perpendicular incidence on the Ni mesh (pictured in SEMs at top) before (dashed trace) and after dipping in hexadecane (solid trace). The transmission resonances are labeled on the before trace. Note the redshift and broadening of the (1,0)\_ resonance after coating with hexadecane, as well as the dips associated with molecular vibrations. (c) The absorption spectrum of the hexadecane film that was extracted from the transmission curve in (b) and an image of a hexadecane molecule.

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FIG. 2. Zero-order transmission spectra at perpendicular incidence of the Ni mesh before (heavy black trace) and after dipping in hexadecane which slowly evaporates (these traces are numbered in time sequence after dipping). The size of the redshift of the (1,0) resonance after coating monotonically depends on the thickness of the coating, so evaporation of the hexadecane film effectively tunes the resonance across the primary hexadecane rocking vibration at  $\sim$ 721 cm<sup>-1</sup>. The other heavy black trace (numbered 35) shows the SP resonance and rocking vibration optimally overlapped.

conduction from the mesh by the metal support. The film typically evaporates until conduction through the support overtakes evaporation leaving a coating of submicron thickness. Traces of the  $(1,0)_{-}$  transmission resonance were recorded before coating and successively in time after coating. Selected traces (numbered in time after coating) are shown in Fig. 2. Reduction in film thickness shifts the initial position of the  $(1,0)_{-}$  primary transmission resonance in this experiment from 628.2  $\text{cm}^{-1}$  with the thickest coating (trace 1) to  $733.8 \text{ cm}^{-1}$  (trace 55) where the film has largely stopped evaporating (the resonance occurs at 754.2 cm<sup>-1</sup> for uncoated mesh). Thickness tuning takes the SP resonance through the most intense CH<sub>2</sub> rocking vibration of hexadecane at 721 cm<sup>-1</sup>. The traces in Fig. 2 were converted to absorption spectra which showed the coating getting smaller in time over most of the spectral region. To account for evaporation, all of the spectra were scaled to give an absorbance of 1.0 for the CH<sub>2</sub> symmetric stretching vibration (plotted in Fig. 3). Also included is a spectrum of hexadecane on ZnSe (heavier trace) as a nonmetallic control. The absorption spectra are nearly identical over most of the range, however, the region overlapped by the  $(1,0)_{-}$  transmission resonance shows variable enhancements, shifts, and line shape changes (versus being on ZnSe) for the prominent  $CH_2$  rocking vibration (expanded in the Fig. 3 inset along with an image of the vibrational motion). Figure 4 shows measurements of the position of the CH<sub>2</sub> asymmetric stretching frequency and the CH<sub>2</sub> rocking frequency as a function of the position of the  $(1,0)_{-}$  SP resonance. The CH<sub>2</sub> symmetric stretch is largely unaffected by the SP showing a shift of  $\sim 0.2 \text{ cm}^{-1}$  from the position on ZnSe (horizontal dotted line). However, the primary CH<sub>2</sub> rocking vibration shows systematic shifts of as much as 3 cm<sup>-1</sup> toward the position of the SP. This is notable because shifts of this size require electric fields on the order of MV/cm in vibrational Stark



FIG. 3. Absorption spectra corresponding to the transmission spectra of Fig. 2. All spectra were scaled to an absorbance of 1.0 on the  $CH_2$  symmetric stretching vibration at 2854 cm<sup>-1</sup>. The  $CH_2$  rocking region has been expanded to see the differences when the (1,0)\_ SP is resonant compared to the spectra on ZnSe. Inset is a picture of the 721 cm<sup>-1</sup> rocking vibration.

effect experiments.<sup>13</sup> There have been a few studies examining surface enhanced IR absorption and SPs (Ref. 14) suggesting that electric fields created by the SPs can be large enough to perturb a molecule at the interface. This general type of interaction has been previously seen with excitonic molecular states and visible SPs [both in SP-ATR (Refs. 9 and 12) and on mesh<sup>15</sup>], as well as between porphyrin molecules and the cavity modes of a semiconductor microcavity.<sup>16</sup>



FIG. 4. Position of two vibrations (CH<sub>2</sub> symmetric stretch and CH<sub>2</sub> primary rock) vs the position of the SP  $(1,0)_{-}$  transmission resonance. The CH<sub>2</sub> symmetric stretch is largely unaffected (top plot) while the CH<sub>2</sub> rock is pulled toward the resonance. The horizontal dotted lines are the positions of the vibrations on ZnSe and the almost vertical dotted line is the position of the SP resonance. The filled symbols correspond to the data set of Fig. 2 which had 28.4% transmission on the  $(1,0)_{-}$  resonance before coating. The open symbols are another data set recorded with a different mesh that had 40.6% transmission before coating. The larger transmission resonance gives a larger effect.

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FIG. 5. Absorption spectra of the  $CH_2$  rocking vibration from transmission data at selected angles of the mesh relative to the incident spectrometer beam of a fixed thickness film of hexadecane. Note that the intensities vary even though the film thickness is constant. The backgrounds were determined by removing a 20 cm<sup>-1</sup> range about the vibration and fitting the remaining portion of the transmission resonance to a ninth order polynomial. The heavier trace corresponds to maximal overlap of the rocking vibration and SP. At 0° the peak is blueshifted, while at 5° and 7°, the peaks are redshifted. All of the mesh line shapes are different than that on ZnSe.

#### ANGLE TUNING

Evaporation effectively halts at some point in the hexadecane experiments and the mesh can be angled relative to the FTIR's incident beam without appreciable change in the amount of absorbing material. Previously, we have observed that if the mesh is angled to disperse the SP transmission resonances,<sup>2,4</sup> the enhanced IR absorption spectrum does not change much in the region from 900 to 3500 cm<sup>-1</sup>, i.e., except the region of the most intense resonance. This previous work shows that one important part of the absorption enhancement is the micron-scale path lengths for absorption enabled by propagating SPs traveling along the surface. Absorption spectra of selected angles are shown in Fig. 6 revealing variations in absorption intensity even though the film thickness is now constant. This suggests a new resonance type of enhancement for mesh-based IR absorption spectroscopy in addition to (and distinct from) the previously identified mechanism of extended absorption path length due to propagating SPs. With angle tuning (as with the thickness tuning), there are vibrational band shifts toward the SP, line shape changes, and peak shifts. The line shapes are generally a few cm<sup>-1</sup> narrower than the full width at half maximum of  $12 \text{ cm}^{-1}$  on ZnSe, with a  $1-2 \text{ cm}^{-1}$  broadening when optimally on resonance with the SP (bold trace in Fig. 5).

# TRANSMISSION RESONANCE SHIFTS AND COATING THICKNESS

Previous experiments<sup>4</sup> have shown that the IR absorption spectrum away from the  $(1,0)_{\pm}$  transmission resonances is largely unaffected by the angle of the mesh to the FTIR's beam. The absorbances in the CH<sub>2</sub> stretch region appear to follow Beer's law and are taken as proportional to hexadecane film thickness. The shifts of both the  $(1,0)_{-}$  and  $(1,0)_{+}$  transmission resonances are plotted versus the absorbance of



FIG. 6. Measured shifts in the  $(1,0)_{-}$  and  $(1,0)_{+}$  transmission resonances with the intensity of the CH<sub>2</sub> asymmetric stretch (proportional to hexadecane film thickness). The solid curves are fits to quadratic polynomials without a constant term, while the dotted curves are similar fits to cubics. Fits of the  $(1,0)_{-}$  data (in cm<sup>-1</sup>) give  $47(8)A+29(8)A^2$  ( $\sigma=6.2$  cm<sup>-1</sup>) and  $94(15)A-85(33)A^2+62(18)A^3$  ( $\sigma=4.5$  cm<sup>-1</sup>) and fits of the  $(1,0)_{+}$  data give  $10(4)A+10(5)A^2$  ( $\sigma=2.1$  cm<sup>-1</sup>) and  $32(6)A-59(16)A^2+49(12)A^3$  ( $\sigma=1.2$  cm<sup>-1</sup>), where A is the absorbance,  $\sigma$  is the estimated standard deviation (e.s.d.) of the fit, and the e.s.d. of the parameters is given in parenthesis as the least significant figure.

the asymmetric CH<sub>2</sub> stretching vibration in Fig. 6. To analyze these results, we resort to an important and informative analogy to wavelength-fixed, angle-scanned SP-ATR experiments.<sup>9</sup> These seemingly different experiments can be quantitatively compared if both are projected to the propagating SP dispersion curve<sup>9</sup> (or curves) in momentum space. Pockrand has given a second order prescription<sup>11</sup> revealing the effects on reflection resonances in SP-ATR experiments of adding absorbing coatings to thin metal films on prisms. The thinness of the metal films ( $d_1$  in Fig. 7, on the order of  $\sim$ 10–50 nm) leads to a splitting of the reflection resonances due to coupling of SPs on each of the adjacent dielectric/ metal interfaces.<sup>17</sup> This coupling leads to extra radiation damping which, in turn, can be affected by coatings. Our mesh has a related coupling between the front and back surfaces as mediated through the holes,<sup>1</sup> although it depends on the thickness of the holes relative to the incident wavelength<sup>18</sup> and may not always be observed. Mesh transmission resonances are labeled<sup>1</sup> by  $(i, j)_{+}$ , where *i*, *j* are steps along the reciprocal lattice (diffraction spots no longer transmitted when SPs are excited) and "±" indicates the symmetric or asymmetric resonance of the split pair [see Fig. 1(b)] associated with front-back coupling. Although the  $(i,j)_+$ resonances of our mesh are considerably less intense than the



FIG. 7. Complex dielectric properties ( $\varepsilon$ ) and geometry (*d* is thickness) of typical SP-ATR setup used in Pockrand's theory for reflection resonance shifts.

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 $(i, j)_{-}$  resonances, they are easier to model because they are not affected by radiation damping and the interaction of coatings with radiation damping. Use of Pockrand's SP-ATR parameters (as defined in Fig. 7: subscripted "1," metal film; "2," coating, and "0" and "3," the surrounding dielectrics) leads to the following relation for frequency shifts in the "+" transmission resonances at perpendicular incidence upon coating and after collecting terms in coating thickness  $(d_2)$ :

$$\Delta \tilde{\nu}_{+} = -C \tilde{\nu}^2 d_2 - D \tilde{\nu}^3 d_2^2, \tag{1}$$

where

$$C = \operatorname{Re}\left\{2\pi\left(1 - i\frac{\varepsilon_{1}''}{2\varepsilon_{1}'}\right)\left(\frac{\varepsilon_{2} - \varepsilon_{3}}{\varepsilon_{2}}\right) \times \left(\frac{\varepsilon_{1}'\varepsilon_{3}}{\varepsilon_{1}' + \varepsilon_{3}}\right)^{2}\left(\frac{\varepsilon_{2} - \varepsilon_{1}'}{\varepsilon_{3} - \varepsilon_{1}'}\right)(-\varepsilon_{1}'\varepsilon_{3})^{-1/2}\right\}$$
(2)

and

$$D = \operatorname{Re}\left\{\frac{4\pi^{3}[((\underline{\varepsilon_{2}}-\varepsilon_{3})/\underline{\varepsilon_{2}})(\varepsilon_{1}'\varepsilon_{3}/(\varepsilon_{1}'+\varepsilon_{3}))^{2}((\underline{\varepsilon_{2}}-\varepsilon_{1}')/(\varepsilon_{3}-\varepsilon_{1}'))(-\varepsilon_{1}'\varepsilon_{3})^{-1/2}]^{2}(2(2\varepsilon_{3}^{2}-\underline{\varepsilon_{2}}^{2})/\varepsilon_{3}(\varepsilon_{3}-\underline{\varepsilon_{2}})+(\varepsilon_{1}'+\varepsilon_{3})/(-\varepsilon_{3}))}{\sqrt{\varepsilon_{1}'\varepsilon_{3}/(\varepsilon_{1}'+\varepsilon_{3})}}\right\}.$$
(3)

The underlined quantities are complex. The values of C and D can be obtained empirically by fitting data of known thickness or theoretically using known values of the dielectric properties. Equations (1)–(3) lay the foundation (or at least suggest the possibility) for using the shifts of mesh transmission resonances to determine the thickness and dielectric properties of thin coatings. It also shows a nonlinear dependence on wavelength which is very different than with fixedwavelength SP-ATR experiments. As an example, consider trace 10 in Fig. 2 which is the first after dipping in hexadecane that reveals the location of the smaller  $(1,0)_+$  resonance. It occurs at 774.4 cm<sup>-1</sup> (a shift of 16.8 cm<sup>-1</sup> from the uncoated position of 791.2 cm<sup>-1</sup>), while the (1,0)<sub>-</sub> resonance occurs at 693.7 cm<sup>-1</sup> (a shift of 60.5 cm<sup>-1</sup> from the uncoated position of 754.2 cm<sup>-1</sup>). A shift of 16.8 cm<sup>-1</sup> for hexadecane on pure Ni ( $\varepsilon_1$ =-2002+*i*1150 at 774.4 cm<sup>-1</sup> from the LD model of Rakic *et al.*,<sup>19</sup>  $\varepsilon_2$ =2.059 for hexadecane, and  $\varepsilon_0$  $=\varepsilon_3=1.000$ ) would be produced by a 755 nm thick coating. Since the Ni is oxidized at the surface, we believe that this represents an upper limit. Characterization (or removal) of the metal's oxide coating will be required for quantitative determinations, but we are now in a position to design experiments that determine coating thickness and dielectric properties. Note that the shift of the  $(1,0)_{-}$  resonance is 3.6 times greater than that of the  $(1,0)_{+}$  resonance, so the radiation damping associated with the front-back coupling through holes of mesh is quite important and can be characterized by comparison to the + resonance behavior. Finally, assuming that absorbance in the CH<sub>2</sub> stretching region is proportional to coating thickness, the  $(1,0)_+$  data in Fig. 6 have been fitted to an Eq. (1)-like form yielding

$$\Delta \tilde{\nu} = (1.5 \pm 0.7) \times 10^{-5} \tilde{\nu}^2 A + (2.3 \pm 1.2) \times 10^{-8} \tilde{\nu}^3 A^2,$$
(4)

where  $\Delta \tilde{\nu}$  and  $\tilde{\nu}$  are in cm<sup>-1</sup> and A is the CH<sub>2</sub> asymmetric stretch absorbance on the peak center. Since the first and

second terms make comparable contributions  $\sim$ 750 cm<sup>-1</sup>, a second order treatment will be needed for shifts of transmission resonances of submicron thicknesses.

## CONCLUSIONS

In addition to the previous enhancements that we have reported associated with the micron-scale path lengths of SPs propagating along the surface, we now show enhancements associated with the interaction of propagating SPs and excited vibrational states. SPs can change the intensity, line shape, and position of a vibrational feature in a traditional FTIR spectrometer. These discoveries required the tuning of SP positions by variation of the coating thickness and angling of the mesh relative to the spectrometer's incident beam. Equations have been presented and initially investigated showing that it is possible to determine the thickness and dielectric properties of thin film coatings on metal mesh with subwavelength arrays of holes.

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