

## COMMUNICATIONS

**Enhanced infrared absorption spectra of self-assembled alkanethiol monolayers using the extraordinary infrared transmission of metallic arrays of subwavelength apertures**

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The surface-plasmon-mediated, extraordinary transmission of metallic arrays of subwavelength apertures has been used as the light source for absorption studies of self-assembled monolayers on metal. Enhanced infrared absorption spectra of a sequence of alkanethiol self-assembled monolayers on copper were recorded for carbon chain lengths varying from 8 to 18 atoms. Transition positions and intensities are presented over a large range of the infrared region. The connection between the vibrational modes of the CH<sub>2</sub> wagging progression and the infinite methylene chain is explored using a traditional coupled oscillator approach and a new cluster perspective. © 2004 American Institute of Physics. [DOI: 10.1063/1.1814052]

The push toward nanoscale assembly fosters a need for simple methods to characterize surfaces. The extraordinary transmission of biperiodic metal meshes<sup>1</sup> has been explored in the infrared (IR) region<sup>2,3</sup> in order to overlap the surface plasmon (SP) mediated phenomena with the fundamental range of molecular vibrations. Enhancements of more than 100-fold in IR absorption by monolayer coatings on the metallic mesh have been observed by analyzing changes in the IR transmission.<sup>2-4</sup> The phrase “extraordinary transmission” refers to the observation that more light is transmitted than is incident upon the apertures of these optically thick meshes, i.e., light that initially strikes optically thick metal is also being transmitted. This behavior is attributed to the excitation of SPs (excitations of the metal’s conducting electrons at the surface) due to the coupling of photons with the subwavelength pattern of perforations. As SPs propagate along the surface, they can tunnel through the apertures and be emitted on the other side of the mesh as photons without being scattered from the incident beam. Since SPs are polaritons (mixed photon-charge oscillation states), it is interesting to consider their interactions with molecules on the surface of the supporting metal as probed by IR absorption.

These experiments start with the finest available commercial mesh from Precision Eforming (Courtland, NY; formerly with Buckbee-Mears Inc.) which is currently only available in Ni. The mesh has a square lattice of square holes (12.7 μm hole-to-hole spacing, 8.0 μm hole width tapering to ~6.5 μm on the opposite side, and 5.0 μm thickness). The Ni mesh is electrochemically coated with copper<sup>3,5</sup> in order to narrow the transmission resonances (enhancing SP lifetimes) and to enable a stable coating of alkanethiol (these coatings are not stable on nickel oxide<sup>6</sup>). This work was accomplished with apertures having widths in the range of 3–6 μm after Cu-coating. The zero-order IR transmission spectrum of a copper coated mesh with ~5.5 μm hole width

is shown with the dotted trace in Fig. 1. Inset is an SEM image of a similarly coated mesh showing the regular square pattern of the mesh. The percentage of open area is 19% and yet the resonance labeled 1,0 shows transmission of 48%, i.e., Ebbesen’s extraordinary transmission effect is exhibited. There are other resonances at higher energies than the 1,0 resonance (such as the one labeled 1,1) that are broader and extensively overlapped leaving a fairly constant transmission of ~5% in the C-H stretching region.

The Cu-coated mesh was dipped<sup>7-10</sup> overnight in 20 mM alkanethiol (hydrocarbon chains terminated on one end with an SH group) in toluene solution and allowed to dry and crystallize for a day. The transmission spectra with an octanethiol coating is given with a solid trace in Fig. 1 (1000 scans, 1 cm<sup>-1</sup> resolution, DTGS detector, 6 hr scan time in a Perkin Elmer Spectrum GX at perpendicular incidence and lattice aligned with spectrometer’s polarization). The alkanethiolate self-assembled monolayer causes a shift in the 1,0 transmission resonance in Fig. 1 which is the wavelength-scanned equivalent of ATR experiments.<sup>11</sup> More importantly, molecular absorptions of the monolayer coating are evident and circled in Fig. 1. In order to convert these signals to an absorption spectrum, points were chosen along the solid trace, excluding the absorption features, and a spline fit was performed to provide a smooth, effective background. Absorption spectra obtained from -log(sample/spline background) are presented in Fig. 2 for a sequence of alkanethiols (C<sub>n</sub>H<sub>2n+1</sub>SH) with carbon chain lengths of  $n_c = 8, 12, 14, 15, 16, \text{ and } 18$  carbons.

There is a great deal of IR work on alkanethiol self-assembled monolayers (SAMs) to guide the interpretation of these spectra<sup>8,12-14</sup> with most work in the C-H stretch region. In our spectra, the absorptions are intense and the peaks are narrow exhibiting full-widths-at-half-maximum of ~4 cm<sup>-1</sup>. Octadecanethiol SAMs on Cu have been assayed

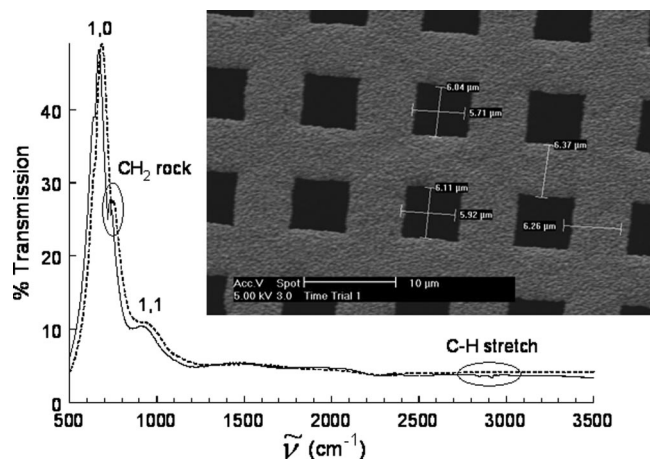


FIG. 1. Zero order, IR transmission spectrum of copper-coated Ni mesh at perpendicular incidence before (dotted trace) and after (solid trace) coating with a self-assembled monolayer of octanethiol. The transmission resonances are labeled (1,0 and 1,1) by steps along the reciprocal lattice vectors. The main resonance shifts red upon coating with the monolayer and molecular absorptions are evident (circled). Inset is a scanning electron microscope image of a similar copper-coated mesh.

with reflection absorption infrared spectroscopy (RAIRS) exhibiting 0.002 absorbances by Whitesides and co-workers,<sup>8</sup> 0.0005 by Ron *et al.*,<sup>10</sup> and 0.001 by Labinis and co-workers<sup>9</sup> in the C-H stretch region. We observe absorbances of  $\sim 0.2$  which are more than 100 times greater than these literature reports. A definitive paper by Whitesides and co-workers<sup>8</sup> states “The low frequency modes, while rich in information, are sufficiently weak in intensity as to preclude quantitative analysis.” Quantitative work with the lower frequency modes is now possible which we demonstrate by examining the CH<sub>2</sub> wagging progression in more detail. The

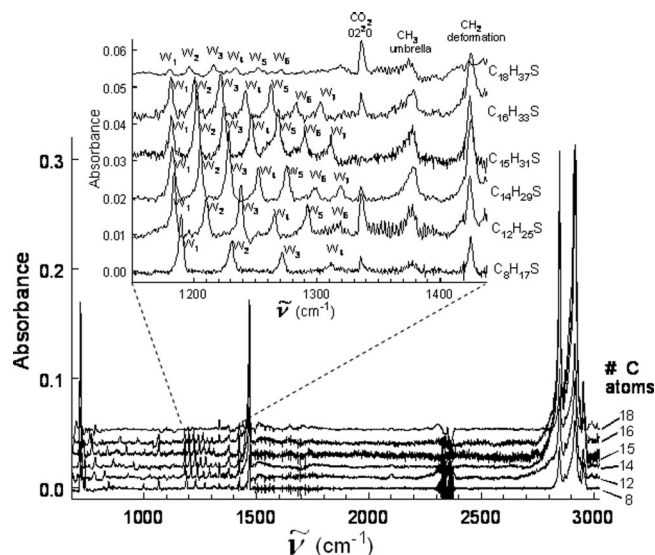


FIG. 2. IR absorption spectra of a sequence of alkanethiol SAMs on copper-coated mesh of carbon chain length increasing from 8 to 18 at room temperature. The absorptions are enhanced by  $>100$ -fold over literature reports. The narrowness of peaks and Snyder's CH<sub>2</sub> wagging and rocking progressions suggest crystalline, all-trans conformations of the hydrocarbon chains. The inset expands the Snyder wagging progression region. All spectra were recorded with 1000 scans at 1 cm<sup>-1</sup> resolution except the top trace which was recorded at 2 cm<sup>-1</sup> resolution 4 months after creation (the longest chain was apparently harder to crystallize).

expanded inset in Fig. 2 shows Snyder's CH<sub>2</sub> wagging progression<sup>15-17</sup> which corresponds to ordered, all-trans chain configurations. This is the first report of the CH<sub>2</sub> wagging progression for alkanethiol SAMs and we are aware of such data for only one other monolayer system, alkanolic acids.<sup>14,18</sup> The peak positions, intensities, and assignments of the observed transitions for the various length alkanethiolate SAMs are presented in Table I. Such information can be used to determine the phase and orientation<sup>13</sup> of the all-trans hydrocarbon chains relative to the surface.

Certain substituent groups of the alkanethiol molecules do not change as the carbon chain length increases, for instance there is always a CH<sub>3</sub> terminating the chain. The CH<sub>3</sub> umbrella vibration occurs at the same frequency with different chain lengths as illustrated in the inset of Fig. 2. Vibrations associated with the wagging motions of a finite methylene chain are described as coupled oscillators and have been related to the wagging of an infinite chain of methylenes.<sup>15,19</sup> Phase differences between adjacent methylenes determine the transition frequencies of finite length chains relative to the infinite chain resulting in smooth changes with chain length, i.e., progressions. Snyder CH<sub>2</sub> wagging progressions are diagnostic for the all trans-conformation. They are labeled with  $W_k$  in the inset of Fig. 2. From a cluster perspective, these vibrations will progress towards the infinite chain wagging frequency as the chain gets longer. Using a strategy often employed in cluster studies, the  $W_k$  frequencies are plotted versus the reciprocal of the number of carbons ( $n_c$ ) in Fig. 3. Noting that an infinite chain has  $1/n_c=0$ , each group of distinct  $k$  value progresses linearly towards a common infinite chain value. A linear least squares routine was used to find the best fit slopes and the common intercept. The fit of all 37 transitions has a standard deviation of 0.7 cm<sup>-1</sup> which is quite acceptable in view of the 1 cm<sup>-1</sup> resolution of the spectra. The slopes are  $148 \pm 6$ ,  $465 \pm 6$ ,  $797 \pm 6$ ,  $1119 \pm 6$ ,  $1448 \pm 8$ ,  $1776 \pm 8$ ,  $2084 \pm 9$  cm<sup>-1</sup> (e.s.d.) for  $k=1$  through 7, respectively, and they change linearly by  $324.5 \pm 1.2$  cm<sup>-1</sup> per  $k$  value as determined by a linear least squares fit of the slopes versus  $k$ . These results offer an alternative to predicting progression frequencies of longer chains, however the data bend away from linearity for shorter chains at higher values of  $1/n_c$ . The common intercept of  $1171.8 \pm 0.5$  cm<sup>-1</sup> (e.s.d.) is very close to the wagging vibrations of 1171 and 1168 cm<sup>-1</sup> observed<sup>20</sup> in several types of polyethylene, which may be taken as a good experimental approximation to an infinite methylene chain.

Methylene wagging progressions are often fit as a function of the phase difference ( $\phi_k$ ) between adjacent oscillators<sup>15</sup>

$$\phi_k = k\pi/(n_c - 1), \quad (1)$$

where  $k$  is the progression index (as used above) and  $n_c$  is the total number of carbons in the chain. Since the denominator is sometimes given as the number of CH<sub>2</sub> groups plus one, note that our use of  $n_c - 1$  is the same quantity where the carbons at each end of the chain are explicitly excluded. A smooth curve of  $\nu_k$  versus  $\phi_k$  results when the progression

TABLE I. Peak positions (in  $\text{cm}^{-1}$ ) and intensities in parenthesis (at maximum in absorbance units) from the IR absorption spectra of alkanethiol self-assembled monolayers on copper-coated mesh. The  $W_k$ s are members of the methylene wagging progression and the  $R_k$ s are of the methylene rocking progression. The rock index is sometimes given by  $n_c-k$  to give better relation to the phase of other vibrations.

Vibration	$\text{C}_8\text{H}_{17}\text{S}$	$\text{C}_{12}\text{H}_{25}\text{S}$	$\text{C}_{14}\text{H}_{29}\text{S}$	$\text{C}_{15}\text{H}_{31}\text{S}$	$\text{C}_{16}\text{H}_{33}\text{S}$	$\text{C}_{18}\text{H}_{37}\text{S}$
$\text{CH}_2$ a stretch	2916.0 (0.0616)	2916.4 (0.0908)	2917.0 (0.2725)	2916.5 (0.3363)	2916.1 (0.2739)	2914.6 (0.0774)
$\text{CH}_2$ s stretch	2847.5 (0.0378)	2848.2 (0.0736)	2848.9 (0.2253)	2848.5 (0.2780)	2848.5 (0.2136)	2848.5 (0.0544)
$\text{CH}_3$ a stretch	2953.5 (0.0235)	2953.0 (0.0256)	2953.5 (0.0610)	2953.8 (0.0677)	2953.2 (0.0458)	2953.2 (0.0088)
$\text{CH}_3$ s stretch	2940.3 (0.0156)		2939.7 (0.0509)	2939.0 (0.0507)		
$\text{CH}_3$ s stretch	2871.5 (0.0123)	2873.2 (0.0312)	2873.8 (0.0698)	2870.6 (0.0737)	2873.2 (0.0597)	2873.6 (0.0115)
$\text{CH}_2$ bend	1468.2 (0.0301)	1469.6 (0.0603)	1470.3 (0.1253)	1469.8 (0.1427)	1470.6 (0.1048)	1470.4 (0.0198)
$\text{CH}_2$ def.	1424.9 (0.0094)	1424.3 (0.0158)	1425.2 (0.0210)	1424.0 (0.0175)	1425.4 (0.0191)	
$\text{CH}_3$ umbrella	1377.5 (0.0028)	1377.5 (0.0082)	1378.0 (0.0084)	1377.5 (0.0096)	1378.4 (0.0093)	1374.4 (0.0039)
$\text{CH}_2$ $W_1$	1189.8 (0.0167)	1184.1 (0.0167)	1182.5 (0.0136)	1181.6 (0.0123)	1181.4 (0.0128)	1180.6 (0.0026)
$\text{CH}_2$ $W_2$	1230.9 (0.0088)	1210.3 (0.0097)	1205.4 (0.0143)	1202.5 (0.0198)	1200.5 (0.0126)	1196.2 (0.0028)
$\text{CH}_2$ $W_3$	1271.9 (0.0064)	1238.3 (0.0136)	1228.4 (0.0181)	1224.1 (0.0159)	1221.9 (0.0135)	1216.0 (0.0034)
$\text{CH}_2$ $W_4$	1311.0 (0.0028)	1265.2 (0.0035)	1252.4 (0.0080)	1246.5 (0.0126)	1242.1 (0.0091)	1233.8 (0.0024)
$\text{CH}_2$ $W_5$		1292.12 (0.0082)	1275.6 (0.0086)	1268.6 (0.0137)	1262.6 (0.0106)	1251.8 (0.0015)
$\text{CH}_2$ $W_6$		1319.0 (0.0037)	1299.4 (0.0026)	1290.0 (0.0095)	1283.4 (0.0059)	1270.7 (0.0018)
$\text{CH}_2$ $W_7$			1319.2 (0.0033)	1311.2 (0.0096)	1303.4 (0.0060)	
C-C stretch	1066.0 (0.011)	1067.5 (0.0074)	1067.4 (0.010)	1067.6 (0.014)	1067.8 (0.0075)	
$\text{CH}_2$ $R_{1,2,\dots}$	719.8 (0.053)	720.4 (0.013)	717.9 (0.048)	719.0 (0.140)	717.9 (0.061)	718.8 (0.021)
$\text{CH}_2$ $R_3$	739.7 (0.022)					
$\text{CH}_2$ $R_5$	844.5 (0.0060)	751.0 (0.0073)	737.4 (0.0073)	733.3 (0.012)	730.7 (0.0050)	
$\text{CH}_2$ $R_6$	923.0 (0.0016)	778.0 (0.0051)	755.6 (0.0014)			
$\text{CH}_2$ $R_7$	999.0 (0.0043)	825.9 (0.0059)	784.6 (0.0080)	769.6 (0.019)	759.3 (0.012)	
$\text{CH}_2$ $R_9$		929.5 (0.0045)	864.9 (0.0068)	837.1 (0.0087)	816.0 (0.0051)	783.8 (0.0023)
$\text{CH}_2$ $R_{10}$			909.9 (0.0015)	889.2 (0.0050)		
$\text{CH}_2$ $R_{11}$			954.9 (0.0044)	922.5 (0.0097)	893.8 (0.0072)	
$\text{CH}_2$ $R_{13}$				1004.4 (0.0043)	973.6 (0.0055)	

is correctly assigned. The curve corresponds to the value of infinite  $\text{CH}_2$  chain wag when  $\phi=0$ . Plots of  $\nu_k$  versus  $\phi_k$  are represented in Fig. 4 for the n-alkanethiol monolayers of this work (black filled circles), n-alkanoic acid monolayers<sup>14</sup> (gray filled circles), n-alkanes<sup>15,16</sup> (open circles, includes missing  $W_1$ s assigned with cluster strategy), n-alcohols<sup>19</sup> (open triangles), and n-alkylammonium salts ( $\text{C}_n\text{H}_{2n+1}\text{NH}_3$ )<sub>2</sub>PbI<sub>4</sub> (Ref. 21) (open squares). The cluster extrapolation result of Fig. 3 has been plotted as a marker for infinite methylene chain with a larger black-filled symbol at  $\phi=0$ . All of these extensive data sets appear to converge to

a similar infinite methylene chain value. The bulk materials (open symbols) cluster around each other and could readily be represented by a single curve. The SAM materials (filled symbols) fall a bit below the bulk data, but exhibit similar general trends. Since monolayers lack some of the intermolecular interactions of three dimensional materials, some differences can be expected. Simple coupled oscillator models (with coupling between the wagging modes only) predict<sup>15</sup> a flattening of the slope of  $\nu_k$  versus  $\phi_k$  curve as  $\phi_k \rightarrow 0$ , however such flattening is not evident in the bulk data sets (although it may be evident in the alkanethiol monolayer

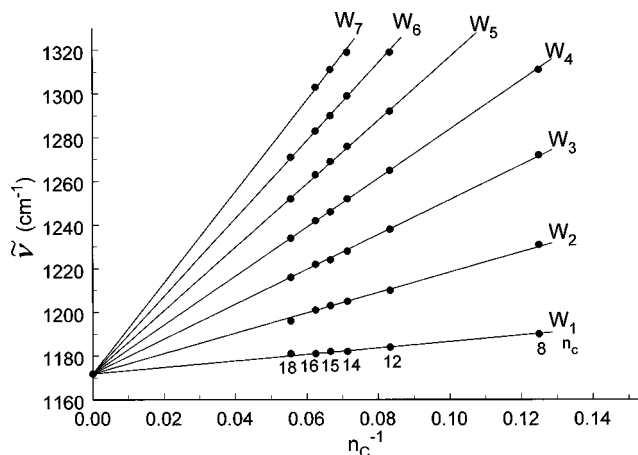


FIG. 3. A plot of the Snyder  $\text{CH}_2$  wagging transition frequencies of alkanethiolate monolayers on copper vs the reciprocal of the number of carbon atoms ( $n_c$ ). Each group of transitions of the same index progress linearly to the same infinite  $\text{CH}_2$  chain value which is in agreement with the  $\text{CH}_2$  wagging frequency observed in polyethylenes. This cluster-based approach provides an alternative to coupled oscillator models.

curve). The data sets in Fig. 4 were fit with a nonlinear least squares routine to the coupled oscillator form<sup>15</sup>

$$\bar{\nu}_{k,n_c} = 1303 \sqrt{a_0 + 2 \sum_{i=1}^k a_i \cos(i\phi_{k,n_c})}, \quad (2)$$

where  $a_0$  is the diagonal element of the Hamiltonian, the  $a_i$ s are the off-diagonal coupling element ( $i$  steps above and below the diagonal), and  $\bar{\nu}$  is in  $\text{cm}^{-1}$ . For instance Snyder's data (with missing  $W_1$ s assigned using the strategy of Fig. 3) gives  $a_0 = 0.953$ ,  $a_1 = -0.012$ ,  $a_2 = -0.060$ ,  $a_3 = 0.022$ , and  $a_4 = -0.013$ , with a standard deviation of  $2.9 \text{ cm}^{-1}$  for 161 transitions as shown by the dotted trace in Fig. 4. The fit

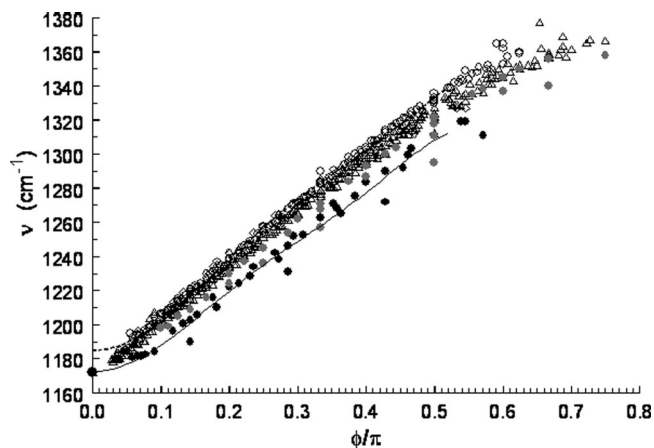


FIG. 4. A plot of the  $\text{CH}_2$  wagging transition frequencies for a variety of long  $\text{CH}_2$  chain systems vs the phase of adjacent oscillators in the methylene chain: alkanethiol SAMs (black filled circles), alkanic acid SAMs (gray filled circles), n-alkanes (open circles), n-alcohols (open triangles), and alkylammonium salts (open squares). The large filled circle at  $\phi = 0$  is the infinite chain value obtained with the cluster approach of Fig. 3. All of these data sets must converge to the wagging transition of infinite  $\text{CH}_2$  chain. The dotted line is a fit of Snyder's n-alkane data to a coupled harmonic oscillator model which curves away from the trend of the data at low  $\phi$  values. The solid curve is a similar fit to the alkanethiol monolayer of this fit which suggests some difference in vibrational coupling of the monolayer vs bulk samples.

bends away from the data at low  $\phi$  values, hence the motivation and/or need for the cluster perspective presented in Fig. 3. The present alkanethiol monolayer data set gives  $a_0 = 0.770$ ,  $a_1 = 0.121$ ,  $a_2 = -0.140$ ,  $a_3 = 0.060$ , and  $a_4 = -0.021$ , with a standard deviation of  $5.1 \text{ cm}^{-1}$  for 38 transitions (the bulk value determined with the cluster approach of Fig. 3 was included) as shown by the solid trace in Fig. 4. Unlike the n-alkane data set, this fit holds at low  $\phi$  values. It appears that the alkanethiol SAMs have more coupling between the wagging vibrations, but there are also couplings with other types of vibrations that are not treated in this model that are likely to be an important factor in the low  $\phi$  trends.

Finally, one further set of observations is presented that speaks to the sensitivity of this new technique. Difficulty was often experienced upon subtracting background gases from these spectra [see the  $\text{H}_2\text{O}(\text{g})$  bending region around  $1600 \text{ cm}^{-1}$  and the  $\text{CO}_2$  asymmetric stretch around  $2330 \text{ cm}^{-1}$ ]. When the mesh was placed in a sample cell and evacuated, this difficulty was eliminated suggesting interaction of the mesh with background gas. There is a very interesting, unidentified peak at  $1337 \text{ cm}^{-1}$  (see the inset of Fig. 2). It lies near the end of the Snyder wagging progression, did not fit the wagging pattern, and did not change with carbon chain length. By scanning these spectra at a resolution of  $1 \text{ cm}^{-1}$  (which is greater than normally employed with condensed samples), a set of evenly spaced transitions ( $\sim 3.1 \text{ cm}^{-1}$ ) was sometimes observed as evident in the dodecanethiolate ( $\text{C}_{12}$ ) trace and to a lesser extent in the octadecanethiol ( $\text{C}_{18}$ ) trace. The peak at  $1337 \text{ cm}^{-1}$  is the  $Q$ -branch ( $\Delta J = 0$ ) in an induced absorption spectrum of  $\text{CO}_2(\text{g})$  by the surface (using  $\nu_1 \nu_2^1 \nu_3$  notation for the vibrational levels, the transition is  $02^2 0 \leftarrow 00^0 0$ ). The lines spaced by  $\sim 3.1 \text{ cm}^{-1}$  (8 rotational constants) above and below the  $Q$ -branch are the  $S$  ( $\Delta J = +2$ ) and  $O$  ( $\Delta J = -2$ ) branches characteristic of Raman transitions or collision induced absorption. This transition is forbidden in gas-phase absorption and not harmonically allowed in Raman spectroscopy. Absorption by  $\text{CO}_2(\text{g})$  is apparently enabled by the intense field of the SPs near the surface. A set of experiments aimed directly at this induced absorption spectrum has been accomplished and will be reported elsewhere shortly.

In summary, we have developed a new spectroscopic technique for detecting molecules on or near a metal's surface. High quality IR absorption spectra of alkanethiol SAMs have been recorded over the full IR range for a sequence of methylene chain lengths. The  $\text{CH}_2$  wagging progressions were particularly striking and have been analyzed in terms of a new cluster approach with regard to their connection to infinite methylene chain and in terms of traditional coupled oscillator methods. The use of SP-mediated extraordinary IR transmission is so sensitive that it can also detect collisions of background  $\text{CO}_2$  with the surface. This method may prove to be a powerful tool in investigating the molecular details of small quantities of a variety of molecules in assemblies built-up from metal surfaces.

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