

Use of the Extraordinary Infrared Transmission of Metallic Subwavelength Arrays To Study the Catalyzed Reaction of Methanol to Formaldehyde on Copper Oxide

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Ordered arrays of subwavelength holes in thin metallic films have been produced that exhibit extraordinary transmission resonances throughout the infrared including the range of wavelengths that excite fundamental molecular vibrations. This phenomenon is attributed to the excitation of surface plasmons which propagate along the surface and tunnel through the holes without being scattered out of an incident beam. Commercial nickel mesh has been coated with copper to reduce the hole size enhancing surface plasmon lifetimes (narrowing resonances) and enabling the study of catalytic processes on the Cu surface. The copper oxide catalyzed reaction of methanol has been studied by recording enhanced zero-order FTIR transmission spectra of the copper mesh activated with a drop of water and then exposed to a drop of methanol. Transformation of $\text{CH}_3\text{OH}(\text{ads})$ to $\text{CH}_3\text{O}(\text{ads})$ and then to the product $\text{CH}_2\text{O}(\text{ads})$ is observed at room temperature and in air with a very simple procedure. The spectrum of adsorbed formaldehyde is analyzed with regard to its orientation on the copper oxide surface.

Introduction

Metallic micro-^{4,5} and nanoarrays⁶ of subwavelength holes 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. Upon coming to a hole, the SPs can tunnel through emerging as photons on the other side of the metallic membrane without being scattered out of the incident beam. We have pushed this effect⁶ into the infrared (IR) spectral region using metallic microarrays in order to match the fundamental range of molecular vibrations. SPs can be excited simply by placing the mesh in the beam path of a traditional, benchtop FTIR spectrometer.⁴ Since long-lived SPs run along the surface of the metal, there is an enhanced effective path length for absorption of IR photons by surface molecular species. Very uniform electrodeposits of copper are applied to the finest commercially available, biperiodic nickel mesh in order to narrow the transmission resonances (increase the SP lifetimes) enabling the spectroscopic study of catalysis on the copper oxide surface.

The effect of hole size on the transmission spectra of these meshes has been studied.⁷ Resonances narrow as the hole size is reduced (SP lifetime increases), but the waveguide transmission threshold also tunes across the IR spectral range diminishing transmission. Hole sizes of $\sim 3\text{--}4\text{ }\mu\text{m}$ present a useful compromise between narrowness of resonance and a useful amount of light. Transmission spectra of a copper-coated mesh ($3.5\text{ }\mu\text{m}$ hole size on a $12.7\text{ }\mu\text{m}$ square lattice) are presented in Figure 1. When first made, the mesh transmits 14.4% of the light on the prominent resonance even though only 7.6% of the mesh is open area; i.e., this spectrum exhibits Ebbesen's extraordinary transmission effect.^{6,8–14} A number of resonances are evident with positions roughly described by the equation inset in Figure

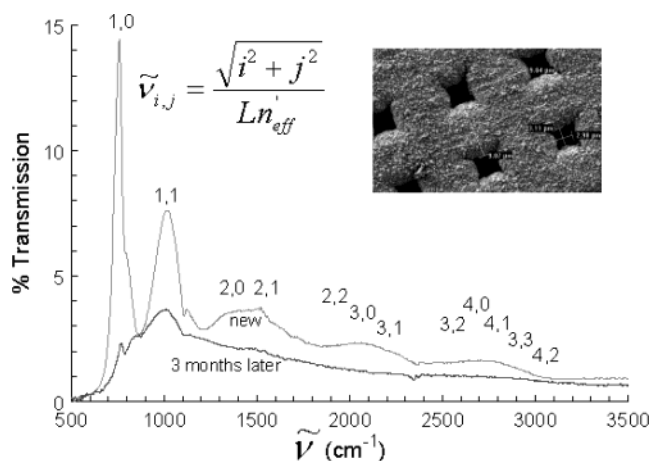


Figure 1. Zero-order transmission spectrum of a mesh with holes closed down to $3.5\text{ }\mu\text{m}$ on a square lattice of spacing $L = 12.7\text{ }\mu\text{m}$. The trace labeled “new” is just after deposition, while the trace labeled “3 months later” is after several months of oxidation in room air. The equation gives the position of resonances where i and j are steps along the reciprocal lattice. Inset is an SEM of mesh similar to the one for which the spectrum was recorded.

1. After many months of exposure to room air, the SP features are diminished as shown by the lower trace in Figure 1. The surface presumably becomes less metallic as it oxidizes and less capable of supporting SPs (when germanium is substituted for metal, the extraordinary transmissions go away^{6,8}). Methanol will stick to copper oxide^{15,16} at room temperature, even though it will not do so on pure copper. Therefore, it was important to have a copper oxide surface in this work as associated with the lower trace of Figure 1. Such a mesh is exposed to a drop of water for activation and then to a drop of methanol. The methanol rapidly evaporates, leaving some methanol adsorbed on the surface which is catalytically converted to formaldehyde on the copper oxide surface. The oxidation of methanol over a

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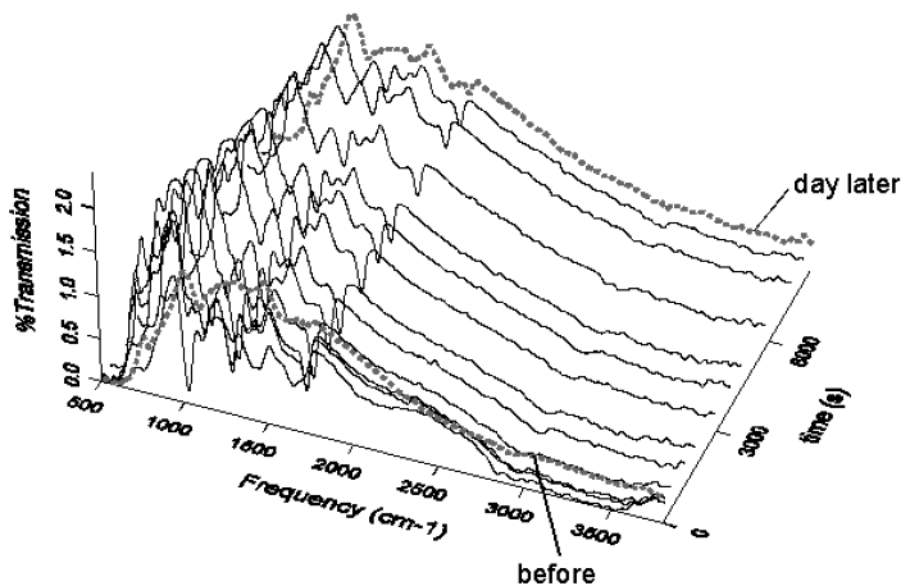


Figure 2. Zero-order FTIR transmission spectra of a copper-coated mesh vs time after exposure to a drop of methanol (after activation with a drop of water). The dotted lines show the spectra of the mesh before and long after exposure. Exposure to methanol increases the transmission of the lowest frequency resonances ($i,j = 1,0$ and $1,1$). The sharper down-going features are molecular absorptions by species on the surface of the mesh.

metal catalyst^{17–19} is a well-known industrial process, and there is a great body of characterizing work.^{15–25} This reaction proceeds through a methoxy radical intermediate at certain temperatures,^{18,19} and the prominent vibrational feature is observed in these studies. Once the product formaldehyde is formed on our mesh surface, it remains detectable for ~ 1 h. The positions and intensities of the observed vibrations are diagnostic for the orientation of this adsorbed molecule on the copper oxide surface.

In the Experimental Section we describe how the mesh was made, how the surface was prepared, and the conditions under which transmission spectra are recorded. Additionally, spectra were recorded at various angles of the mesh with the incident spectrometer beam because the SP background changes with angle while absorptions are expected to remain constant. This allows better distinction of dips between SP resonances and molecular absorptions. In the Results section, absorption spectra are extracted from the various transmission curves and absorption spectra are examined versus time. At longer times, when the formaldehyde spectrum changes slowly, similar absorption spectra are extracted from different angle transmission spectra providing consistency. The intensities and positions of adsorbed formaldehyde vibrations are tabulated for analysis in terms of orientation on the surface. Conclusions are reached about the orientation of formaldehyde on the copper oxide surface with regard to the forbidden component of vibrations parallel to the metal surface. In the Discussion, the >100 -fold enhancements in absorbance are compared to competing techniques, comparisons are made to formaldehyde on other surfaces, and the prospects of working with other metals and other surface molecules are considered.

Experimental Section

We invented a method to uniformly close down the hole widths of fine commercial mesh by electrochemical deposition of copper. A roughly 5×5 mm² piece of Ni mesh (Precision Eforming, 2000 lines/in. electroformed, $12.7 \mu\text{m}$ hole-to-hole spacing on a square lattice, $6.7 \mu\text{m}$ square holes, $5 \mu\text{m}$ thick) is spaced by ~ 2 mm from a ring-shaped Cu electrode (8 mm o.d. and 2 mm i.d.) 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 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 to $<1 \mu\text{m}$ by varying the deposition time. A mesh with $3.5 \mu\text{m}$ holes was chosen for these experiments. A scanning electron microscope (SEM) image of a similar mesh is shown in the inset of Figure 1. Statistics gathered in other experiments revealed variations of about $\sim 0.2 \mu\text{m}$ in the hole size. The resulting meshes are rugged and easy to handle.

To obtain catalytic surfaces of high activity, the mesh was exposed to room air for a few weeks until its transmission spectrum looked like the lower trace in Figure 1. It is well-known that oxygen is required to activate a copper surface for catalysis,^{18,26} so we waited for the development of a copper oxide surface. A zero-order FTIR transmission spectrum was recorded with the mesh at incidence perpendicular to the beam of a Perkin-Elmer Spectrum GX FTIR spectrometer as shown by the dotted trace at the beginning of Figure 2. Next, a drop of water was applied to the mesh to activate the surface. This water wash was important because it made our signals stronger and more reproducible. It presumably adds hydroxyl groups to the surface, which improves the probability of methanol reacting.^{19,21–23,26–32} It took about 10 min for the transmission spectrum to return to its pre-water form. Then, a drop of methanol was applied to the mesh, which was quickly (in ~ 10 s) placed back in the FTIR spectrometer. The liquid methanol was gone in a few seconds (the time it took to get the mesh into the FTIR spectrometer) as verified by the wavering of HeNe laser diffraction spots in other experiments. Consequently, any observed absorptions are due to adsorbed or reacted methanol. Successive IR transmission spectra were recorded at a resolution of 32 cm^{-1} with 40 scans averaged so that a whole spectrum could be acquired in ~ 10 s, enabling us to follow the kinetics. Spectra were sequentially recorded for the first 2 min and then less frequently over several hours. The transmission spectra vs time are shown in Figure 2. Application of methanol produced a large and reversible increase in the light transmitted at the 1,0 and 1,1 resonances. The origin of this effect is not currently understood, but the application of methanol made the transmis-

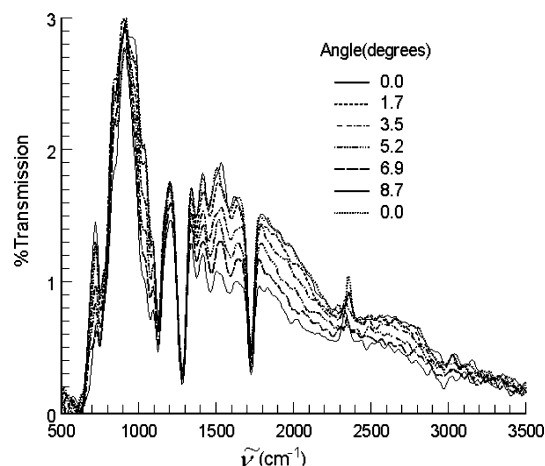


Figure 3. Zero-order transmission spectra recorded at different angles of the mesh relative to the incident beam at ~ 14.4 min after exposure to methanol. The adsorbed formaldehyde was slowly changing at this point. The SP profiles disperse, i.e., the background changes with angle, while the molecular absorptions remain at fixed wavenumbers.

sion spectra like the lower trace in Figure 1 become more like the upper trace in Figure 1, i.e., temporarily similar to a less oxidized surface. In addition, molecular absorptions are evident in the resonant profiles. After 1 day, the transmission spectrum returned to its pre-methanol appearance and the experiment could be repeated.

The changing background of the surface plasmon resonances is problematic for the goal of extracting absorption spectra from the data in Figure 2. It can be difficult to distinguish the dips between resonances from absorptions, so a strategy was devised to disperse the transmission resonances by changing the angle of the mesh relative to the incident light beam. The lattice of the mesh was aligned with the spectrometer's polarized electric field, such that rotation about this axis investigated transverse magnetic (TM) polarization in the ΓX direction of the square lattice (this geometry produces the largest movement of SP resonances with angle). Noting that the chemistry subsides after a few minutes leaving signals of an adsorbed product that persist for about an hour, transmission spectra were recorded rapidly (~ 10 s each) at successive angles (0.0° , 1.7° , 3.5° , 5.2° , 6.9° ,

and 8.7°) about each of five different average times of 5.5, 14.4, 28, 45, and 57 min. Transmission spectra centered around the time of 14.4 min are presented in Figure 3. There are definitive changes in the profile of the SP resonances, while the prominent absorption features remain at constant positions. In the next section we describe how absorption spectra were extracted from transmission profiles. We used data vs angle to see if the absorption spectra changed when the SP resonances moved.

Results

To extract absorption spectra from the data in Figures 2 and 3, points were chosen along the trace excluding the positions of the absorption features. A spline fit was accomplished with these points providing a background for the positions with absorption features. Absorption spectra are presented in absolute absorbance units (AU) as $-\log(\text{sample}/\text{background spline})$ vs time in Figure 4. Since the methanol evaporates within a few seconds of its application, all of the absorption features shown in Figure 4 pertain to adsorbed species on the copper oxide surface.

In the first spectrum at 27 s, we see a large peak at 1028.9 cm^{-1} with an absorbance of 0.92 AU, which corresponds to absorbing 88% of the light (about 100 times greater than high quality literature spectra¹³³). Both adsorbed methoxy and methanol have many similar vibrational peaks, but different intensities. The adsorbed methoxy [$\text{CH}_3\text{O}(\text{ads})$] spectrum is dominated by the 1028 cm^{-1} $26,30,33-36$ transition. Saturation in the OH stretching region of the first spectrum precludes a determination of $\text{CH}_3\text{OH}(\text{ads})$ vs $\text{CH}_3\text{O}(\text{ads})$, but the $\text{CH}_3\text{OH}(\text{ads})$ is gone by the second spectrum at 41 s. At times of 27, 41, 56, and 71 s, the peak occurs at 1028.9, 1025.0, 1024.3, and 1022.2 cm^{-1} , respectively, and the absorbance is 0.92, 0.86, 0.51, and 0.15 AU, respectively. The peak shifts as it diminishes, and such concentration dependence has been previously observed for $\text{CH}_3\text{O}(\text{ads})$.^{30,33} The intensity vs time does not fall as an exponential (as for a reactant), but takes the bell-like shape of an intermediate species. Consequently, the early absorption spectra are dominated by methoxy adsorbed on copper oxide.

The $\text{CH}_3\text{O}(\text{ads})$ spectrum is replaced by a product spectrum of adsorbed formaldehyde [$\text{CH}_2\text{O}(\text{ads})$] after ~ 1 min. The

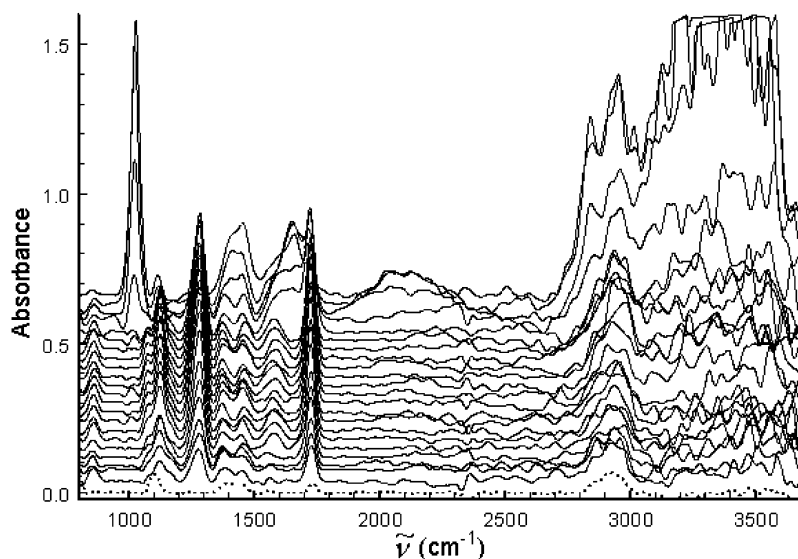


Figure 4. Absorption spectra vs time after exposure of mesh to methanol showing the transformation from adsorbed methoxy to formaldehyde. The spectra are offset for better viewing. The times from top trace to bottom are 27, 41, 56, 71, 85, 100, 115, 130, 145, 162, 203, 303, 419, 765, 1167, 1732, 2843, 3678, 4343, 5752, 7247, and 8000 s. The dotted (bottom) trace corresponds to 23 h and is similar to the spectrum before exposure. It shows the size of difficulties in distinguishing absorptions from SP resonance features with this method.

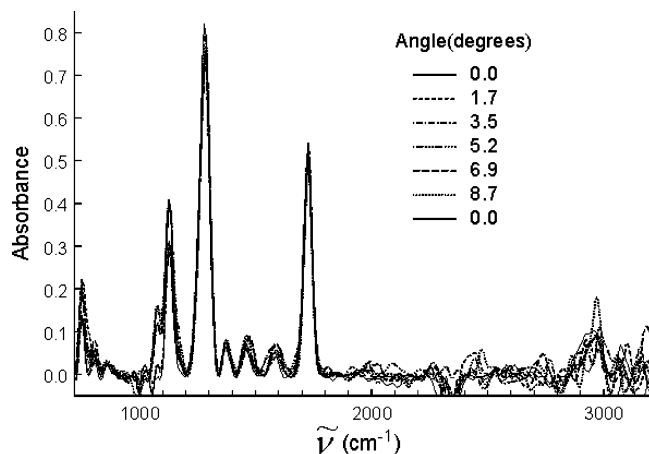


Figure 5. Absorption spectra of formaldehyde on copper oxide about 14.4 min after exposure to methanol at various angles of the mesh relative to the spectrometer beam.

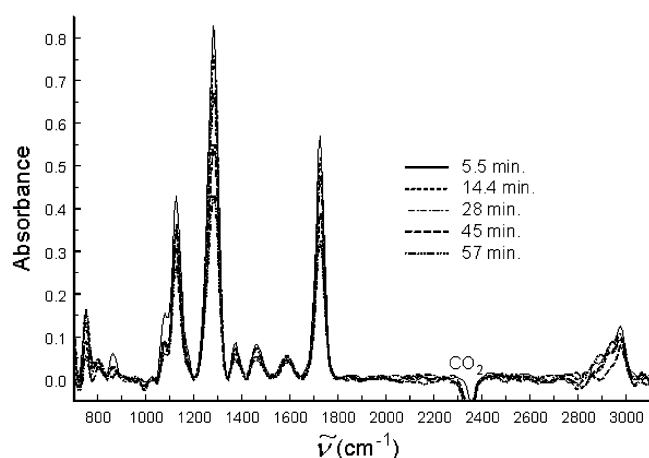


Figure 6. Absorption spectra of formaldehyde on copper oxide vs time after exposure to methanol. Each trace is an average of many spectra recorded at different angles of mesh relative to the spectrometer beam.

formaldehyde adsorbed on copper oxide has prominent features at 1726 cm^{-1} ($\text{C}=\text{O}$ stretch) and 1283 cm^{-1} (CH_2 rock). There is a rise of $\text{CH}_2\text{O(ads)}$ correlated with the fall of methoxy and then a slower reduction on the time scale of 1 h associated with desorption from the surface. Since the $\text{CH}_2\text{O(ads)}$ spectrum changes on a slower time scale, the whole procedure was repeated. At an average time of 14.4 min, a sequence of transmission spectra were recorded at 0.0° , 1.7° , 3.5° , 5.2° , 6.9° , and 8.7° of the spectrometer's incident beam to the direction perpendicular to the mesh as shown in Figure 3. Variation of this angle causes the SP transmission resonances to shift their position. Absorption spectra obtained in the same manner as previously described (spline background) were obtained from each trace and are presented in Figure 5. These absorption spectra are generally quite consistent. Places where the spectrum is not consistent, such as just below 1100 cm^{-1} , show where the background spline procedure has trouble distinguishing structure in a transmission resonance from a molecular absorption feature. This procedure worked well and these spectra were averaged to give one spectrum characteristic of the average time. The angle variation experiment was performed at 5.5, 14.4, 28, 45, and 57 min after exposure to methanol. The averaged spectra are presented in Figure 6. They show consistent spectra diminishing in time. These vibrational transitions and intensities for formaldehyde on copper oxide, as well as corresponding gas-phase assignments and intensities, are presented in Table

TABLE 1: Assignments of Vibrational Peaks of Formaldehyde Adsorbed on Copper Oxide along with Gas-Phase Results for Comparison

vibr of CH_2O (ads) (cm^{-1})	rel int by integrated area	corresponding gas-phase assign	vibr of $\text{CH}_2\text{O(g)}^a$	gas-phase int ^b (km/mol)
751.3(6)	0.11(4)			
1127.6(3)	0.27(5)	ν_4 CH_2 out-of-plane bend	1167	6.5(6)
1283.8(4)	1.000	ν_6 CH_2 rock	1249	9.9(10)
1373.2(6)	0.070(4)			
1459.6(16)	0.089(7)	ν_3 CH_2 bend	1500	11.2(10)
1589.4(13)	0.072(16)			
1726.8(3)	0.60(3)	ν_2 $\text{C}=\text{O}$ stretch	1746	74(5)
		ν_1 CH_2 sym stretch	2782	76(7)
		ν_5 CH_2 asym stretch	2843	88(8)
2971(16)	0.32(14)	$\nu_2 + \nu_6$		

^a 1–3. ^b 2.

1. This information is useful for determining the orientation of the formaldehyde on the surface.

Discussion

The transition intensities and positions in Table 1 offer some clues as to the orientation of formaldehyde on the copper oxide surface. The underlying metallic nature of the surface allows only vibrations with components perpendicular to the surface to be seen. There have been studies on the orientation of different intermediates and products of the oxidation of methanol on copper surface.^{26,36,37} If the formaldehyde lies flat on the surface, then vibrations perpendicular to the surface will be favored, while vibrations within the plane will be suppressed. The lack of observed CH_2 stretches and the maximum intensity of the CH_2 rock argue for a formaldehyde that is largely parallel to the metal surface. The band at 1726.8 cm^{-1} indicates a $\text{C}=\text{O}$ group which is red-shifted relative to the gas phase by an amount similar to the $\text{CH}_2\text{O}\cdots\text{HBr}$ complex (1727.9 cm^{-1}), suggesting that the formaldehyde is hydrogen bound to an OH group on the surface (recall that the surface was activated with water). The $\text{C}=\text{O}$ vibration has intensity comparable to the intensity of the ν_4 and ν_6 out-of-plane vibrations; however, in the gas phase it is 7–10 times more intense. Therefore, its intensity suggests that the molecule is not perfectly flat. These intensities might be used to get an average angular deviation of the formaldehyde's C_2 -axis from the plane. We do not believe that the molecule is rotated far from planarity about its C_2 -axis or the CH_2 bend would be more intense. In lieu of more rigorous calculations, the $\text{CH}_2\text{O(ads)}$ appears to be a hydrogen bound species lying nearly flat on surface.

There are observed peaks in our absorption spectra that have not been identified yet. These peaks may be combination and/or overtone bands with low-frequency vibrations of $\text{CH}_2\text{O(ads)}$, or they may arise from other reaction pathways available for this reaction.³⁸ The abundance of methoxy radical in Figure 4 argues that the methoxy pathway is predominant, although there could be small amounts of some other product such as formate. Previous kinetics studies²⁰ also see the methoxy pathway as most probable and predict trends similar to those generally seen in this work. Our $\text{CH}_3\text{O(ads)}$ decays faster than the model predicts,²⁰ and our formaldehyde is formed a bit earlier than predicted. Perhaps these differences are due to the activation with water, which implies a role for OH groups on the surface (i.e., a different activation site), or perhaps the system has more reaction steps than are being taken into account.

The vibrational spectra of both gas-phase and adsorbed methoxy radical have been well characterized.^{26,30,31,33–36,39} Previous spectra of the adsorbed methoxy intermediate were

recorded by reflection absorption infrared spectroscopy (RAIRS)^{26,30,33,35,39} under very controlled conditions. Half monolayers of the methoxy intermediate in this process show absolute absorbances in RAIRS^{26,30,33,39} of ~ 0.004 (at reduced temperatures that make the transitions narrower). Here we have an absolute absorbance >0.9 ! A more quantitative assessment awaits further work due to currently uncharacterized parameters associated with percent coverage, line width narrowing associated with comparison at reduced temperatures, surface roughness (similar enhancements are seen with uncoated mesh of nanoscale flatness^{4,40,41}), and the common (but not necessarily equal) contribution of the well-known surface enhanced infrared absorption (SEIRA)^{42–44} effect for molecules on metals as mediated by metal oxides and surface roughness. The current work exhibits a great enhancement in IR absorption that could be used to record spectra of chemical processes previously considered too difficult for direct absorption.

Striking features of this work include absorbances that are more than 100 times greater than literature values, a submonolayer amount of adsorbed methoxy radical that is absorbing 88% of the light, and a coating of the surface with methanol that increases the surface plasmon mediated transmission. The spectroscopic properties of the mesh combined with the chemical ability to load the mesh with methoxy radicals (easily detectable in direct absorption for ~ 60 s at room temperature!) present many possibilities. The unusual IR transmission and long SP lifetimes of these metallic meshes allow various adsorbed species to be studied with unusually high fractional absorptions using a commercial, tabletop FTIR spectrometer at room temperature and in air. Other alcohols, such as ethanol and benzyl alcohol, also show this type of behavior. By working in the infrared, a number of other metals including W, Ni, Pt, Pd, and Cr could also be used and might be of catalytic interest.

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