

The First Raman Spectrum of an Organic Monolayer on a High-Temperature Superconductor: Direct Spectroscopic Evidence for a Chemical Interaction between an Amine and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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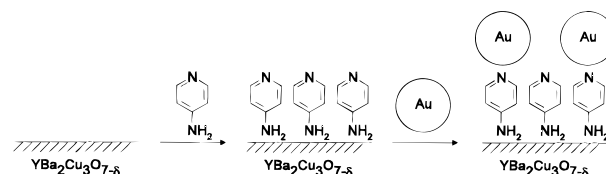
Received July 25, 1996

Since the first reported example of the preparation of an organic monolayer on a cuprate-based high-temperature superconductor (HTSC),¹ a great deal has been learned about the utility of these new surface structures for tailoring HTSC surface and interfacial properties. Monolayers on HTSCs have been used as hydrophobic layers for corrosion passivation² and as prelayers for polymer adhesion² and nucleation.³ In addition, they have been used in attempts to prepare a new class of artificial tunnel junctions for studying the fundamental physical properties of the HTSCs.⁴ Although the modes of adsorbate surface binding are still undetermined, it is known that alkylamines, arylamines, alkylthiols, alkyldisulfides, and alkylselenols spontaneously adsorb onto the surfaces of a wide range of cuprate superconductors to form robust monolayer films.^{1b}

Although organic monolayers on HTSCs have been characterized by a series of surface analytical techniques,^{1–3} vibrational spectroscopic methods, which have been crucial to the characterization of other monolayer structures, have yet to be reported for this class of monolayer. Because of its extraordinary sensitivity, surface-enhanced Raman spectroscopy (SERS) has been extremely useful in characterizing monolayer structures on a variety of substrates with accessible surface plasmon resonances, including Au, Ag, and Cu.⁵

Herein, we report a method to do SERS on cuprate superconductors modified with organic monolayers. Using this method, we have obtained the first direct spectroscopic evidence for a chemical interaction between an arylamine and the underlying cuprate superconductor. This method takes advantage of the work of Natan and Murray involving the use of colloids⁶ and evaporated metal films,⁷ respectively, to enhance the Raman spectra of organic films on a variety of substrates. Natan has shown that Au and Ag nanoparticles will assemble onto surfaces with the appropriate organic functionality to yield SERS-active substrates.⁶ The Natan method has been used to gain spectroscopic information regarding organic thin films that were subsequently deposited onto the layer of colloid particles. Apparently, under the conditions employed, the underlying organic monolayer is never spectroscopically observed. Similarly, Murray has shown that Ag metal can be vapor-deposited onto monolayers to gain spectroscopic information regarding

Scheme 1



the underlying organic structure.⁷ Our method, which is a modification of the Natan method and designed to be compatible with the hygroscopic nature and chemical reactivity of the HTSC, yields outstanding Raman spectra of many organic monolayers on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Furthermore, these spectra can be collected from a commercially available FT-Raman spectrometer with a Nd:YAG laser ($\lambda_{\text{ex}} = 1064 \text{ nm}$, $\sim 70 \text{ mW}$), making it a very versatile and straightforward approach for the study of organic monolayer films on HTSCs.

The schematic representation of the monolayer preparation and colloid self-assembly process is shown in Scheme 1. First, a monolayer of 4-aminopyridine is formed on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by immersion of the HTSC in a 1 mM acetonitrile solution of the adsorbate molecule. This molecule was chosen because it has one functional group, an arylamine, that is proposed to have a chemical affinity for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and a pyridine group that is expected to have an affinity for Au colloids. Both of these assumptions are verified spectroscopically (*vide supra*) and by prior electrochemical data which suggests that the pyridine group *does not* have an affinity for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ under these conditions.^{1b} Once the monolayer is formed, its exposure to a solution of Au colloids is expected to result in the adsorption of colloids and the formation of a SERS-active surface.

Unlike the other substrates studied thus far for monolayer purposes,^{8ab} $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is water sensitive and corrodes in air to form an insulating layer of $\text{Ba}(\text{OH})_2$, which subsequently reacts with CO_2 to form BaCO_3 .⁹ This process not only is damaging to the superconductor but it also degrades, and eventually, desorbs the monolayer. To circumvent this problem, Au colloids ($5 \pm 2 \text{ nm}$) were prepared and dispersed in toluene in the absence of stabilizing alkylthiol.¹⁰ The 5.2 mM colloid solution was subsequently used to modify the HTSC surface-immobilized monolayers, Scheme 1. In toluene solution, the UV-vis spectra of the dispersed colloids exhibit a characteristic absorption band at 520 nm, but when aggregated, this band is red-shifted and responsible for their SERS activity.⁵

In our first experiment, which was designed to test the suitability of the proposed method (Scheme 1), a polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ pellet¹¹ was treated with a 1 mM acetonitrile solution of 4-aminopyridine. After soaking the substrate for 48 h, the electrode was thoroughly rinsed with acetonitrile, and the Raman spectrum of the chemically modified surface was acquired. No signal associated with the monolayer was detectable (Figure 1A). Significantly, when the same substrate was immersed in a solution of Au colloids for 2 h and then rinsed several times with pentane to remove the physisorbed colloids,

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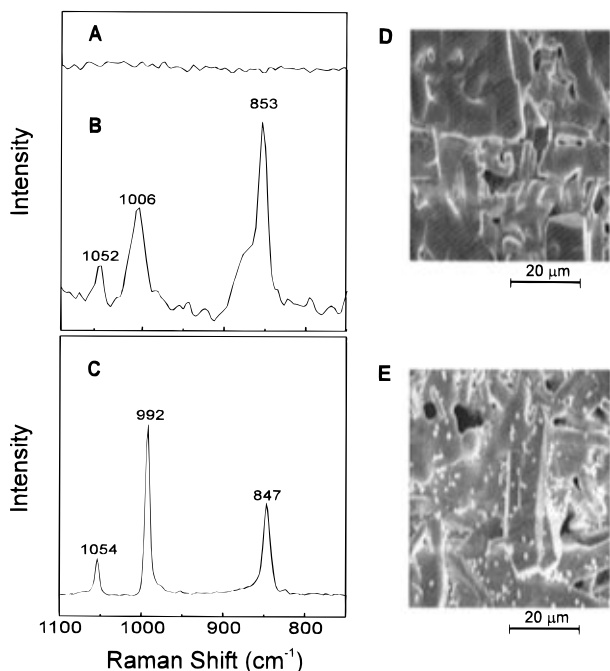


Figure 1. The Raman spectra for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ modified with a monolayer of 4-aminopyridine: (A) before treatment with Au colloids (band pass, 4 cm^{-1} , integration time, 160 s) and (B) after 2 h treatment with Au colloids (band pass, 4 cm^{-1} , integration time, 320 s). (C) The Raman spectrum of solid 4-aminopyridine (band pass, 4 cm^{-1} , integration time, 20 s). SEM photographs of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ modified with a monolayer of 4-aminopyridine: (D) before treatment with Au colloids, and (E) after soaking in the Au colloid solution for 2 h (white spots are colloid aggregates).

a Raman spectrum with an excellent signal-to-noise ratio was obtained (Figure 1B), which compared well with the spectrum of solid 4-aminopyridine (Figure 1C). The assembly of the Au colloids on the HTSC/monolayer surface was confirmed by scanning electron microscopy (SEM), which clearly shows the surface adsorption of the colloidal particle aggregates (compare panels D and E, Figure 1). Note that the surface coverage of the colloids is soaking-time dependent and, therefore, controllable. Indeed, when the same substrate is soaked in the colloid solution for an additional 12 h, increased colloid surface coverage is observed by SEM. Three strong bands were observed in the $1100\text{--}750\text{ cm}^{-1}$ region of the SERS spectrum of the 4-aminopyridine monolayer (Figure 1B). On the basis of the band assignments made by Spinner for solid 4-aminopyridine,¹² we assign the two monolayer bands centered at 1006 and 1052 cm^{-1} to the ring-breathing and deformation modes of the pyridinal ring, respectively. The out-of-plane C–H bending vibration mode also is observed at 853 cm^{-1} .^{12a}

Importantly, new information about HTSC monolayers can be obtained via the SERS methodology reported herein. By deuterium labeling the amine group of the 4-aminopyridine, adsorbing the deuterated 4-aminopyridine onto $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and characterizing it via SERS, we were able to identify the NH_2 scissoring band for the monolayer at 1625 cm^{-1} (Figure 2). This band, which appears at 1654 cm^{-1} in the Raman spectrum of solid 4-aminopyridine (Figure 2A), experiences a 29 cm^{-1} shift upon adsorption onto $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Figure 2B). Note that these bands were unambiguously assigned to the NH_2 scissoring mode as they experience the expected shift to lower energy when labeled with deuterium (Figure 2C,D). The shift of the NH_2 scissoring band upon adsorption is indicative of the strong chemical interaction between the amine moiety and the underlying HTSC.

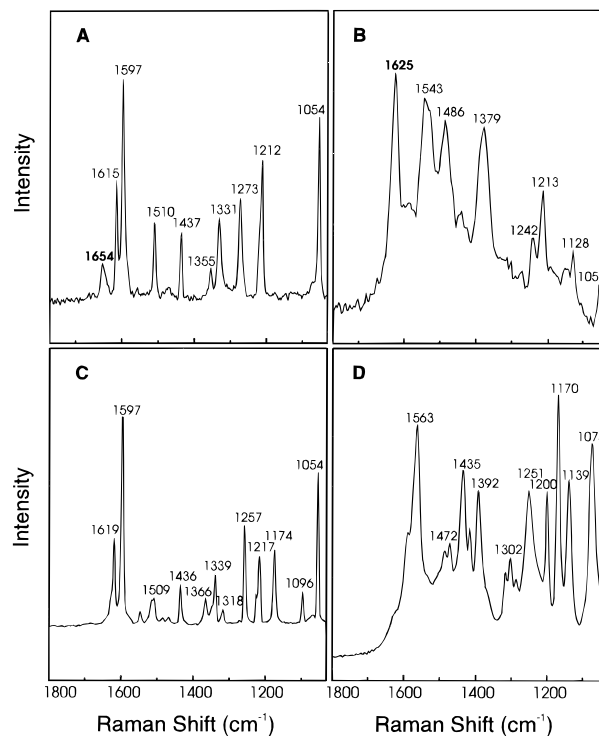


Figure 2. The Raman spectra of (A) solid 4-aminopyridine (band pass, 4 cm^{-1} , integration time, 20 s) (NH_2 scissoring mode in bold, 1654 cm^{-1}), (B) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ modified with a monolayer of 4-aminopyridine (band pass, 4 cm^{-1} , integration time, 320 s) (note the NH_2 scissoring mode at 1625 cm^{-1}), (C) solid N-deuterated 4-aminopyridine (band pass, 4 cm^{-1} , integration time, 20 s) (note the disappearance of the band at 1654 cm^{-1} when compared with the Raman spectrum of the unlabeled material, see A), and (D) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ modified with a monolayer of N-deuterated 4-aminopyridine (band pass, 4 cm^{-1} , integration time, 320 s) (note the disappearance of the band at 1625 cm^{-1} when compared with the Raman spectrum of the unlabeled material).

To make sure that all of the bands in the monolayer spectra were due to the 4-aminopyridine and not the Au colloids or the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, a similar set of spectroscopic experiments were carried out with a monolayer of $\text{NH}_2(\text{CH}_2)_{10}\text{NH}_2$, a molecule with very low Raman cross section bands. This film, which also binds Au colloids, exhibits one barely detectable band centered at 1100 cm^{-1} in the $1800\text{--}750\text{ cm}^{-1}$ region of the spectrum in the presence of colloids and no bands in the absence of colloids. This experiment shows that under these conditions (1) the Raman spectrum of the 4-aminopyridine monolayer (Figure 1B) is not complicated by the Raman spectra of the colloids or HTSC and (2) the spectroscopic signal for the monolayer is benefitting from the choice of the large Raman cross section of the 4-aminopyridine adsorbate molecule.

This work (1) documents the first vibrational spectroscopic study of a monolayer on a cuprate superconductor, (2) extends the utility of Au colloids as Raman enhancement tools to the important class of cuprate HTSCs, and (3) provides the first evidence for the direct interaction between the amine group of an adsorbate molecule and the underlying HTSC surface. It is likely that this approach can be used to determine the chemical nature of the adsorption of adsorbate molecules with functional groups other than amines on HTSCs.

Acknowledgment. C.A.M. acknowledges the NSF Science and Technology Center for Superconductivity and the AFOSR for support for this work. C.A.M. also acknowledges use of the NU MRC (Award no. DMR-9120521). Professors J. T. McDevitt, K. R. Poeppelmeier, D. J. Schiffrin, and R. P. Van Duyne and Mr. D. J. Campbell are acknowledged for helpful discussions.

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