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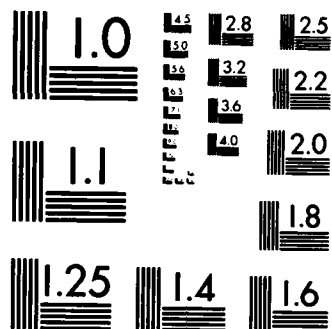
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The reactions of C_2H_2 and CH_3C_2H
on Ag Powder

by

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¹M.A. Barteau and R.J. Madix, Surf. Sci., 115, 355 (1982).

²J.M. Vohs, B.A. Carney, and M.A. Batreau, *J. Am. Chem. Soc.*, **107**, 7841 (1985).

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THE REACTIONS OF C_2H_2 AND CH_3C_2H ON Ag POWDER

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ABSTRACT

Ag powder is activated by pulsing it with NO_2 gas which forms fresh Ag microclusters. This powder is then exposed to subsequent pulses of C_2H_2 or CH_3C_2H (3.7% in N_2). The surface enhanced Raman scattering (SERS) spectra show dramatic intensity variations due to rapid changes in adatom concentration. Normalization of these time-dependent SERS spectra to the background scattering intensity, which is proportional to the adatom concentration, provides spectra which represent adsorbate coverage if major surface reconstruction does not occur. The temporal development of the SERS spectra of C_2H_2 shows rapid degradation with no evidence for adsorbed species. In contrast, propyne reacts more slowly, as evidenced by the behavior of the intensity at 1980cm^{-1} due to adsorbed $-C_2-$. The reactions observed are in accord with the models developed by Barteau and Madix[1] and Vohs, Carney, and Barteau[2]. Exposure to both alkynes results in the appearance of SERS active NO, an adsorbant not previously observed at room temperature. Ellipsometric measurements are consistent with the presence of a carbon overlayer, which may stabilize the NO and render the system inert to further chemical reaction.

INTRODUCTION

The reactions of acetylene on oxygen-covered Ag metal have been elucidated in the last few years using ultra high vacuum (UHV) spectroscopic techniques. A review of Ag surface chemistry has been published recently[3]. At low temperatures, the surface oxygen abstracts a H from C_2H_2 to form adsorbed HC_2 and OH. As the temperature is increased, the adsorbates recombine to form C_2H_2 , which is desorbed, and C_2 species, which form surface C matrices upon further heating.

Previous studies of the SERS spectra of acetylene adsorbed on Ag are limited to pure Ag surfaces in UHV systems. The spectra of C_2H_2 on cold evaporated Ag films at 120K are characterized by peaks at $171(\nu_{Ag-C_2H_2})$, $635(\nu_4, \Pi_g)$, $756(\nu_3, \Pi_u)$, $1934(\nu_2, \Sigma_g^+)$, $3245(\nu_3, \Sigma_u^+)$, and $3317(\nu_1, \Sigma_g^+)\text{cm}^{-1}$ [4]. The strongest characteristic, the peak at $\sim 1934\text{cm}^{-1}$, is assigned to the $C\equiv C$ stretching mode. In gaseous C_2H_2 , this mode occurs at 1974cm^{-1} .

Recently, the reaction mechanism of NO_2/N_2O_4 gas pulses on oxygen-covered Ag metal powder has been reported[5]. The oxygen-covered surface reacts with NO_2 to form $AgNO_3$, and the Ag metal forms $AgNO_2$. As time evolves, the $AgNO_2$ undergoes an autocatalytic reaction to form Ag, $AgNO_3$, and NO gas. The Ag imbedded in the $AgNO_3$ migrates to sites where Ag_n microclusters are formed. These microstructures are a necessary part of the SERS enhancement mechanism. They are also highly reactive towards additional pulses of gases, even though they are imbedded in a $AgNO_3/AgNO_2$ matrix. This paper reports the results of the reactions of C_2H_2 and CH_3C_2H gas pulses with Ag_n microstructures prepared by exposing a Ag surface to a pulse of NO_2/N_2O_4 gas at room temperature. It is shown

that: 1) the reactions occur rapidly and are in accord with the results obtained under UHV conditions, 2) the alkynes form additional Ag microstructures which augment the intensity of the SERS signal. 3) the intensity of the SERS background increases several fold, indicative of a corresponding increase in the surface concentration of adatoms. The implication is that the background signal may be used to monitor the contribution of the charge transfer mechanisms to the total SERS intensity.

EXPERIMENTAL

The SERS experimental apparatus, described previously[5], permits the measurement of Raman scattering spectra over a range of $100\text{--}2600\text{cm}^{-1}$ in 1s intervals with a S/N of ~ 100 . Gas pulses are typically 5s wide and the volume is adjusted to correspond to an exposure of 5L for the Ag powder used ($0.6\text{m}^2/\text{gr}$). No attempt was made to pre-clean the Ag powder surface, which is exposed to ambient conditions and presumed to be covered with oxygen and carbon compounds.

The ellipsometric measurements are also described earlier[5]. Evaporated Ag mirrors, $\sim 1000\text{\AA}$ thick, were exposed to $\text{NO}_2/\text{N}_2\text{O}_4$ prepared from Cu and concentrated HNO_3 . The gases were dried by passage over CaSO_4 and carried into the ellipsometric cell by N_2 gas. A AgNO_3/Ag matrix $\sim 80\text{\AA}$ thick was thereby generated. Propynyl lithium was reacted with water and the resulting propyne gas was dried and carried into the cell by N_2 gas.

RESULTS

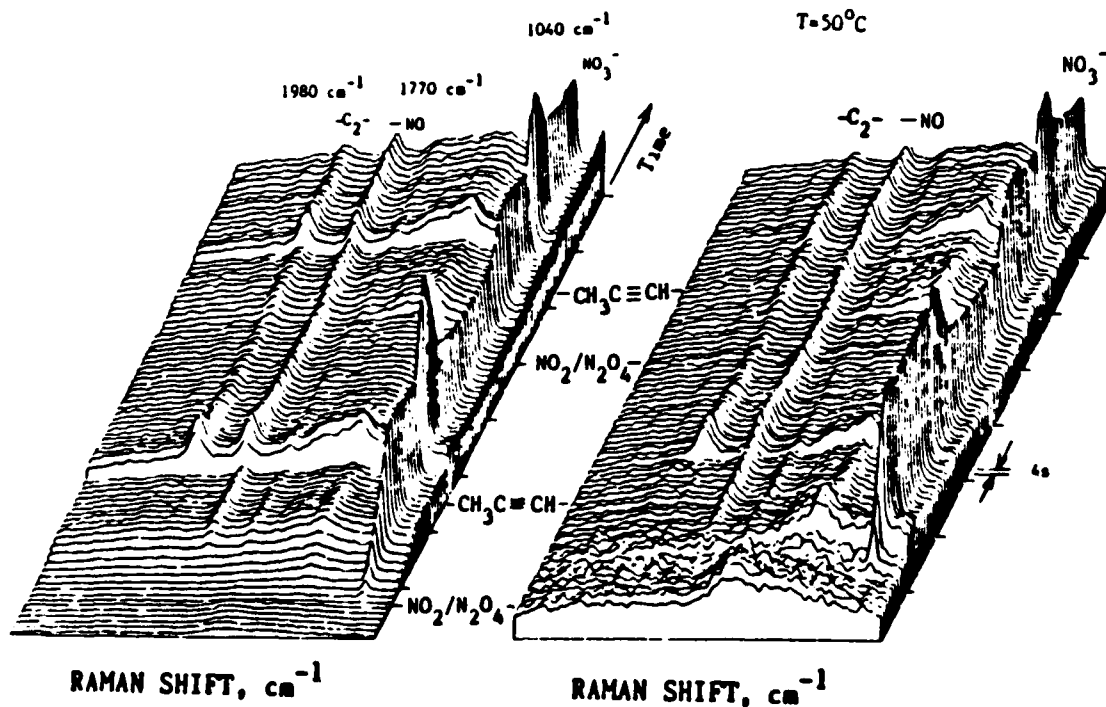


Figure 1: a) SERS spectrum using a sequence of $\text{NO}_2/\text{N}_2\text{O}_4$ followed by $\text{CH}_3\text{C}\equiv\text{CH}$. $\lambda=514\text{nm}$, $P=10\text{mw}$, and $\Delta t=4\text{s}$. No signal messaging. b) Spectrum after normalization to the background intensity at the highest frequency shift shown for each frame.

The time-dependent SERS spectra of propyne on Ag powder are shown in Figures 1a and 1b. Figure 1a is the spectrum as recorded with an optical multichannel detector. Figure 1b shows the same data, but each frame is normalized to the average photon count at $\sim 2100\text{cm}^{-1}$, just beyond the portion of the spectrum arising from the $\text{C}\equiv\text{C}$ vibrational mode at 1900cm^{-1} .

Consider the intensity of the peak at 1040cm^{-1} due to the symmetric stretch of NO_3^- adsorbed on Ag[5]. In the first step, $\text{NO}_2/\text{N}_2\text{O}_4$ gas forms AgNO_2 which covers the Ag surface. The AgNO_2 undergoes autocatalytic decomposition into AgNO_3 , Ag, and NO. As this process occurs, Ag microclusters are formed, causing an increase in surface "roughness" and a corresponding increase in the SERS signal. There are two primary mechanisms that control the SERS enhancement. One is the electromagnetic enhancement, which relies upon the presence of Ag particles about 20nm in radius[6]. The other mechanism is due to a charge transfer process which depends upon the formation of Ag adatoms, or clusters of a few Ag atoms, on the surface. The SERS enhancement factor is $\sim 10^4$ for the electromagnetic mechanism and ~ 100 for the charge transfer mechanism[7].

Figure 1a shows that the background signal increases after the addition of NO_2 . It is generally accepted that this scattering is due to electron-hole recombination processes, similar to those of the charge transfer enhancement mechanism, that occur when a metal is irradiated with laser light[8]. The intensity of the background may serve as a measure of the contribution of the charge transfer mechanism to the overall SERS enhancement. Thus, if the overall gain is

$$G(t) = G_{EM}(\omega_L, \omega) G_{CT}(\omega_L, \omega) G_{other}(\omega_L, \omega) \Theta(t),$$

then

$$G(t)/G_{CT}(\omega_L, \omega) = G_{EM}(\omega_L, \omega) G_{other}(\omega_L, \omega) \Theta(t)$$

where $G_{EM}(\omega_L, \omega)$ is the electromagnetic enhancement factor, $G_{CT}(\omega_L, \omega)$ is the adatom enhancement factor, $G_{other}(\omega_L, \omega)$ is any other enhancement mechanism, and $\Theta(t)$ is the coverage[9]. If the background for a given spectral frame is measured at a wavelength away from any vibrational peaks, and if this background is used to normalize the rest of that spectral frame, the result is a SERS spectrum arising from electromagnetic enhancement alone. Figure 1b is an example of such a spectrum.

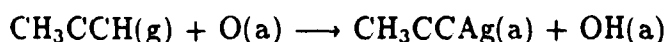
This analysis is true only if the heat of reaction does not reconstruct the Ag surface, destroying the 20nm scale "roughness". Figures 2a and 2b illustrate the effect of surface reconstruction on the SERS spectra with a pulse sequence of $\text{N}_2\text{O}/\text{N}_2\text{O}_4$ followed by C_2H_2 . Although the overall spectrum (Figure 2a) shows dramatic changes in the intensities of both the background and the peaks, the electromagnetic spectrum (Figure 2b) is nearly featureless. Thus, it appears that the intensity fluctuations are largely reflections of the transient concentration of adatoms.

The reactions of $\text{CH}_3\text{C}\equiv\text{CH}$ with Ag have been studied extensively[2]. An oxygen-covered Ag metal surface is a strong base that not only abstracts the acidic H to form $\text{CH}_3\text{C}\equiv\text{C}(\text{a})$, but also forms the propargyl radical, $\text{CH}_2\text{C}\equiv\text{CH}(\text{a})$, and $\text{OH}(\text{a})$. At 300K, these molecules dissociate on the surface to form adsorbed C and H. The H(a) reacts with OH(a) to form H_2O .

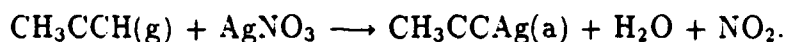
Figure 1b shows SERS spectra obtained as these reactions occur on Ag microclusters. After the initial pulse of $\text{NO}_2/\text{N}_2\text{O}_4$, the rapid growth of the NO_3^- peak at 1040cm^{-1} occurs, as well as a slow growth of a peak at 1771cm^{-1} . Upon exposure of this surface to a pulse of propyne, a strong peak appears at 1979cm^{-1} . This peak is assigned to the

stretching mode of $\text{C}\equiv\text{C}$ [4]. A strong increase in the nitrate and carbon signals from $\sim 1300\text{cm}^{-1}$ – 1500cm^{-1} also occurs, indicating that some of the $\text{CH}_3\text{C}\equiv\text{C}$ degrades. Finally, the peak at 1771cm^{-1} has grown strong and remains with a nearly constant intensity while the intensities of the $\text{C}\equiv\text{C}$ and NO_3^- peaks decrease.

The following sequence of reactions is in agreement with those observed under UHV conditions and can provide an explanation of the spectra shown in Figure 1. These reactions occur on the same Ag microclusters responsible for the SERS enhancement. Upon exposure to CH_3CCH , two reactions occur immediately:



and



The second reaction explains the decrease in the intensity of the SERS signal due to NO_3^- upon initial addition of CH_3CCH . The growth of the CH_3CCAg peak at 1979cm^{-1} is rapid, but because the CH_3CCAg slowly decomposes to form adsorbed C and H, this $\text{C}\equiv\text{C}$ bond signal nearly disappears before the addition of a second pulse of $\text{NO}_2/\text{N}_2\text{O}_4$ causes a regeneration of the surface.

The peak at 1771cm^{-1} is assigned to a nitrosyl group by comparison of known frequency shifts of nitrosyl-metal compounds. It is apparently stabilized by the presence of the acetylide decomposition products. The peak does not appear unless acetylide is present. Though NO is produced during the autocatalytic decomposition of AgNO_2 —the reaction that initially forms the Ag microclusters—no $\text{NO}(\text{a})$ was ever observed[5]. With each pulse of CH_3CCH , this peak shifts by $\sim +5\text{cm}^{-1}$ then returns to 1771cm^{-1} .

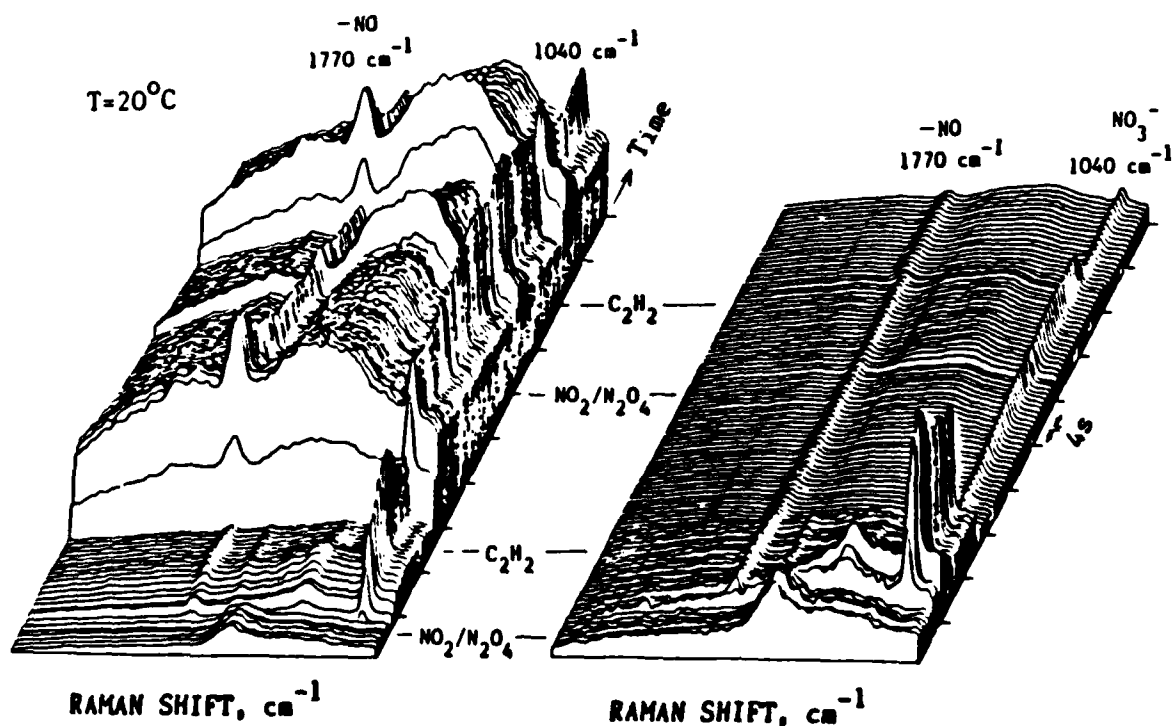


Figure 2: a) SERS spectrum obtained during an experiment identical to that of Figure 1 except that C_2H_2 was used in place of $\text{CH}_3\text{C}\equiv\text{CH}$. b) The same spectrum after normalization.

Figure 2 shows spectra obtained for the reaction of acetylene with Ag microclusters produced, again, by a pulse of NO_2 gas on Ag powder. The reactions are notably different from those of propyne. No peak arising from the $\text{C}\equiv\text{C}$ moiety is observed. Copious adatoms are produced photochemically as AgNO_3 reacts with both acidic hydrogens on acetylene. Also, acetylene reacts with the oxide-covered Ag forming adsorbed OH and carbon. The only peak in Figure 2 resulting from the acetylene reaction is the NO peak at 1771cm^{-1} . As before, this peak shifts in frequency when acetylene is added but, in this case, the shift is $+25\text{cm}^{-1}$. It appears that the addition of acetylene causes a positive polarization of adsorbed NO. The reason for the change in surface charge is not clear, but perhaps depends upon the presence of an adsorbed C overlayer, rapidly produced in the chemical reaction.

Spectra of reactions involving deuterated acetylene and propyne showed no isotopic shifts except for a CH peak at $\sim 3000\text{cm}^{-1}$, which is commonly observed.

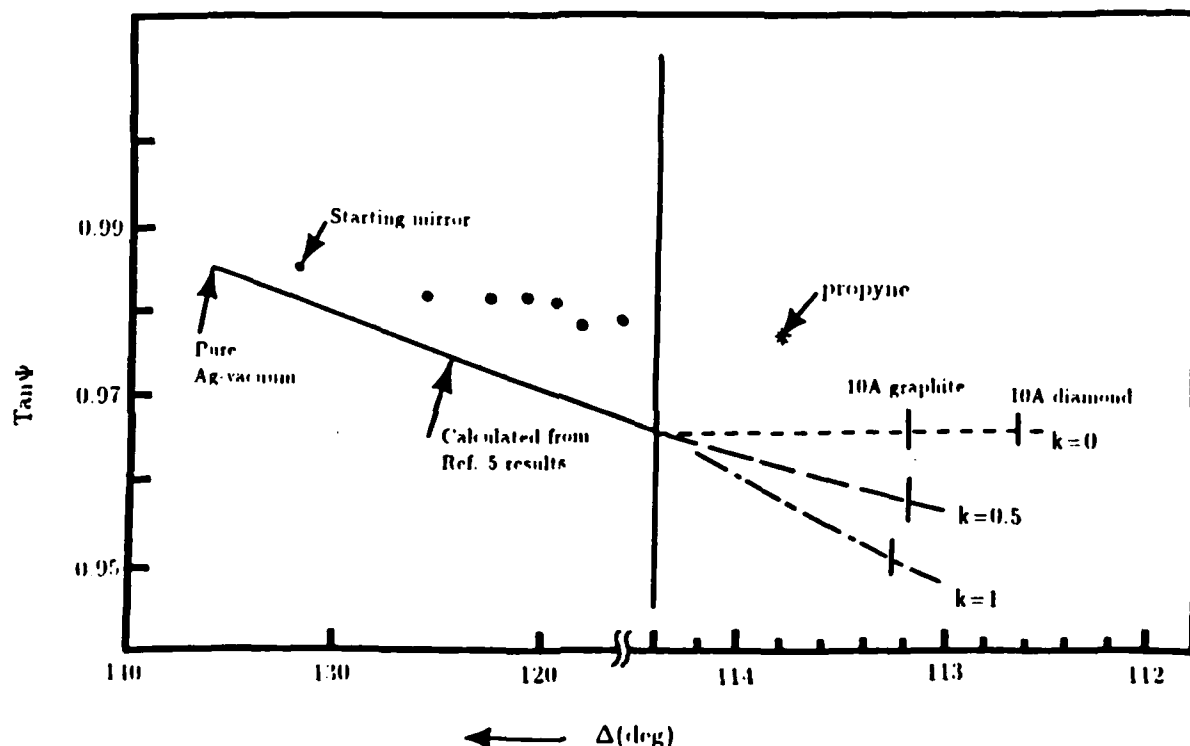


Figure 3: The experimental ellipsometric results for the growth of a film on a Ag mirror after treatment with NO_2 gas followed by CH_3CCH compared with three different models of the surface.

Figure 3 shows the computed ellipsometric angles, Ψ and Δ , for a diamond layer, a transparent graphite layer, and absorbing graphite layers, all formed on a Ag substrate with an 80A AgNO_3/Ag matrix overlayer. The following optical constants were used to perform the ellipsometric calculations: $N_{\text{Ag}} = 0.082 - 3.61i$ [10], $N_{\text{AgNO}_3/\text{Ag}} = 3.311 - 0.1068i$ [5], $N_{\text{DIAMOND}} = 2.4235$ [11], $N_{\text{GRAPHITE}} = 1.918, 1.918 - 0.5i$, and $1.918 - i$, and $N_{\text{AMBIENT(AIR)}} = 1$. The experimental points to the left of the solid vertical line correspond to exposing the Ag mirror to $\text{NO}_2/\text{N}_2\text{O}_4$. The first point represents the Ag mirror with its intrinsic film of oxygen and carbon compounds. The point to the right of the vertical line shows the result of exposure to propyne. Once the carbonaceous overlayer formed, it did not seem capable of further growth with continued exposure to propyne. The propyne

exposure was ~ 70 (490mL at STP) times as great as the $\text{NO}_2/\text{N}_2\text{O}_4$ exposure (7mL at STP). Nevertheless, the carbon layer formed by degradation of the propyne was only on the order of 5Å. These observations are in accord with the SERS results reported here and with the reaction scheme that has been proposed by previous investigators.

CONCLUSION

The results presented in this paper indicate that normalization of SERS spectra may be a useful procedure for the study of surface chemical reactions. Additional results from a variety of surface chemical measurements are necessary to support this conclusion. It was also shown that the reactions of alkynes on Ag powder at room temperature are rapid and passivate the surface to further chemical reaction due to formation of a carbon overlayer. Finally, as previously suggested[5], it appears that the addition of $\text{NO}_2/\text{N}_2\text{O}_4$ forms catalytically active Ag_n microstructures which are useful in the study of Ag surface chemical reactions.

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