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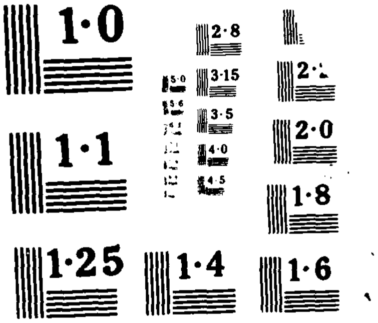
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Surface Enhanced Raman Scattering Applied to Surface Chemical Kinetics

by

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The application of SERS to study surface chemical reaction kinetics is presently limited because the enhancement mechanisms are reaction dependent. That is, the size and the number density of the surface roughness is dependent on the reaction parameters, such as H and temperature that are functions of time. For selected reactions, a partial solution exists if during the course of the reaction, surface reconstruction is confined to modification of the adatom structures. Electromagnetic enhancement, due to surface roughness of 20nm, is nearly constant in this case, and only the adatom enhancement mechanism is time dependent. The adatom concentration is also proportional to the background intensity due to electron-hole recombination in the metal substrate. Thus the adatom time dependence of the SERS spectra may be removed by normalization to the background in a spectral region without discrete SERS peaks. Applications to the decomposition of allynes, phosphonates, and NO_2 on Ag powders provide supportive evidence.

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SURFACE ENHANCED RAMAN SCATTERING APPLIED TO SURFACE CHEMICAL KINETICS

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ABSTRACT

The application of **SERS** to study surface chemical reaction kinetics is presently limited because the enhancement mechanisms are reaction dependent. That is, the size and the number density of the surface roughness is dependent on the reaction parameters, such as ΔH and temperature that are functions of time. For selected reactions, a partial solution exists if during the course of the reaction, surface reconstruction is confined to modification of the adatom structures. Electromagnetic enhancement, due to surface roughness of $\sim$20nm, is nearly constant in this case, and only the adatom enhancement mechanism is time dependent. The adatom concentration is also proportional to the background intensity due to electron-hole recombination in the metal substrate. Thus the adatom time dependence of the **SERS** spectra may be removed by normalization to the background in a spectral region without discrete **SERS** peaks. Applications to the decomposition of allynes, phosphonates, and NO_2 on silver powders provide supportive evidence.

INTRODUCTION

Surface enhanced Raman scattering, (**SERS**), has the potential to be powerful tool in the study of surface chemical reaction processes. Sensitive to less than monolayer coverage even under ambient conditions, **SERS** has been used to obtain detailed surface reaction kinetics in only a few cases [1,2]. Instead, the main research emphasis has been to characterize adsorbates on metal substrate surfaces and to elucidate the mechanism of the enhancement factors (10^4 to 10^6). Even though it has been more than a dozen years since the effect was accidently discovered[3] during which time many ingenious experiments have been performed, the details of the contributions to the enhancement are still unclear.

Two major contributions are evident[4]:

1) The electromagnetic enhancement and
2) The chemical or charge transfer enhancement.

While other processes have been proposed [4], the evidence is less compelling and the contributions may be small.

The overall enhancement factor is assumed to be the product of the various enhancement mechanisms:

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

where $G_{EM}(\omega_L, \omega)$ is the electromagnetic enhancement, $G_{CT}(\omega_L, \omega, t)$ is the charge transfer enhancement, $G_{other}(\omega_L, \omega)$ is any other enhancing parameter, and the adsorbate coverage is $\theta(t)$.[5]

Is is interesting to consider the surface heating effects on each of the enhancement terms. Since $G_{CT}(\omega_L, \omega, t)$ depends on the presence of small clusters of the metal substrate (adatoms), it will be more strongly affected by the reconstruction of the surface due to the heat of the surface reaction ΔH. On the other hand $G_{EM}(\omega_L, \omega)$ is more stable towards annealing, and will be unaffected by reasonably small ΔH. Thus if an independent measurement of $G_{CT}(\omega_L, \omega)$ is available, then $G(t)$ can be normalized to that measurement to obtain a parameterized spectral intensity, $G(t)/G_{CT}$, which is proportional to $\theta(t)$ under these conditions.

Electromagnetic Enhancement: The need for the electromagnetic enhancement mechanism is based on the experimental observation that the metal substrate surface must be roughened. This may be achieved by formation of metal island films, electrochemical deposition, metal vapor deposition on rough substrates such as CaF_2, and chemical reactions in which etching or metal deposition occurs. Colloidal metal systems which give strong SERS signals have also been extensively studied.

Colloids have an advantage in that they are convenient model systems for any surface roughness if it is assumed that roughness is approximated by a collection of spherical particles either singly or on a metal surface. An incident electromagnetic wave, E_{inc}, will induce a multipole charge distribution on a metal sphere of complex dielectric constant, ϵ. This results in a local field, E_L, which may be calculated from the Lorentz-Mie theory:

$$E_L \sim \frac{\epsilon - n^2}{\epsilon + 2n^2} \cdot E_{inc}$$

For silver spheres imbedded in water with an index of refraction,n, E_L is very large because the real part of the dielectric constant of Ag is negative in the visible spectral region. If the surface of the sphere is covered with an adsorbate,the large value of E_L manifests itself in an apparent large polarizability of the adsorbate, and hence a large Raman cross section. Extensive calculations show that E_L is maximized at $\lambda_{inc} \sim 400$ nm and a particle size $\sim$ 20 nm and exceed E_{inc} by a factor of 1500 in the case of Ag [6,7]. For

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Cu and Au spheres, the factor is reduced to ~ 100 and the particle size maximum occurs at 22 nm. For many other metals, the imaginary part of the dielectric constant, which is the loss component,is very large in the spectral region usually employed in Raman scattering, and the EM enhancement factor is greatly reduced in magnitude.

Charge Transfer Enhancement: If monochromatic light impinges on a metal surface, a broad band emission is observed which has been shown to be a luminescence rather than a Raman process[8]. The phenomenon has been ascribed to the excitation of electrons into energy level above the Fermi level. Both in the excitation and in the electron hole recombination process, momentum and energy is transfered to small clusters of metal atoms on the surface called adatoms.

If a molecule is adsorbed on the metal, then the energy diagram is as shown in Fig. 1. The process is the same as with the metal luminescence except after the creation of the hole-electron pair, there is a finite probability that the electron can tunnel through the barrier shown to form the adsorbate negative ion for a few vibrations. The electron may also tunnel back through the barrier and recombine with the hole. If, however, the neutral is molecule is left in an excited vibrational state, the emission upon recombination of the electron hole pair will occur at a frequency shift equal to the vibrational energy of the adsorbate molecule. Model calculations have estimated that the enhancement from this mechanism is $\sim 10^2$ to 10^3.[9]

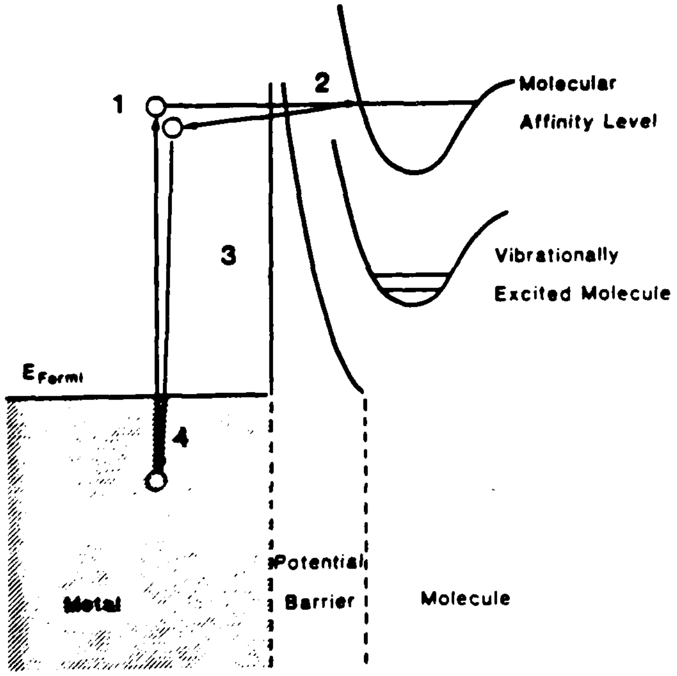
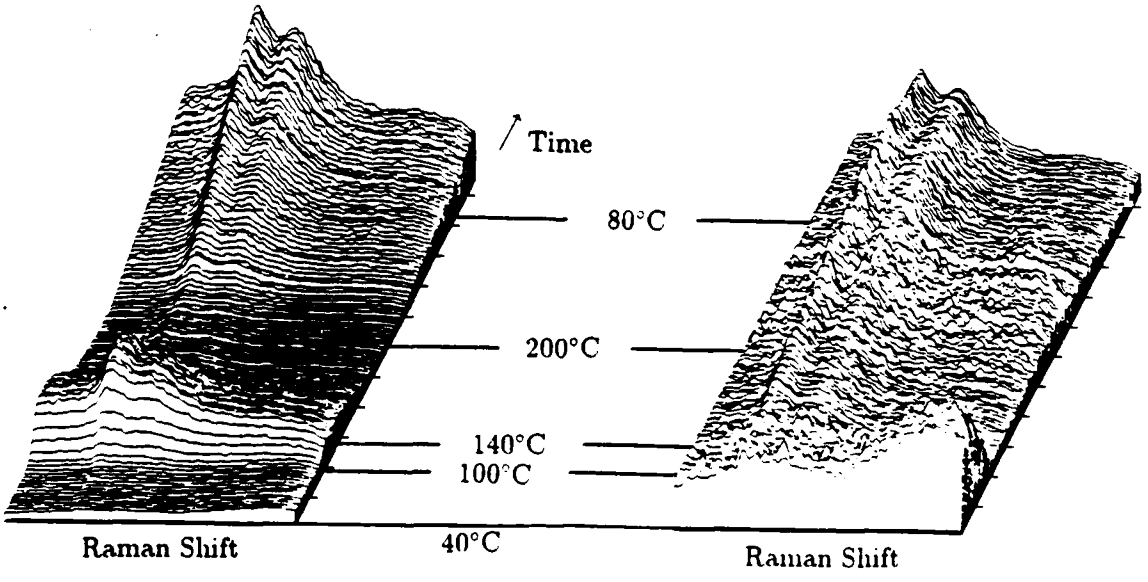


Figure 1

EXPERIMENTAL

Example I. When Ag powder ($\sim 0.5\mu$) which has been previously exposed to ambient conditions is heated in nitrogen gas to 200°C, a **SERS** spectrum is observed in the spectral region from 1200 to 1500 cm^{-1}. The broad bands have been ascribed to surface carbon species[10]. As the temperature is raised, the intensities of the peaks increase, reaching maxima at 140°C before disappearing at 200°C. Figure 2a shows that upon cooling, the spectra reappears strongly. Figure 2a also shows that the background signal intensity, I_{back} mimics the **SERS** signal intensity, I_{SERS}. If I_{SERS}/I_{back} is calculated for each spectral frame, the resulting spectrum exhibits no remarkable temperature dependence as shown in Fig. 2b.

It is known that carbon on Ag is difficult to remove thermally in an inert atmosphere in this temperature range, and the coverage should therefore be reasonably constant. Thus it appears that the background intensity, which is proportional to the adatom concentration, may be used to normalize the total enhancement to the charge transfer mechanism to obtain a modified **SERS** signal is due to the surface concentration of adsorbates $\theta(t)$ and the relatively temperature insensitive electromagnetic enhancement mechanism.



SERS

Figure 2a

Normalized **SERS**

Figure 2b

Example II. We have previously reported [1] that NO_2/N_2O_4 gas pulses on Ag metal powders produce **SERS** signals at 1040cm^{-1} and 819cm^{-1} due NO_3^- and NO_2^- adsorbed near the Ag microstructures formed in the reaction sequence:

$$\begin{gathered} Ag_2CO_3 + NO_2 \longrightarrow AgNO_3 + CO_2 \\ Ag + NO_2 \longrightarrow AgNO_2 \\ 2AgNO_2 \longrightarrow AgNO_3 + NO + Ag \\ nAg \longrightarrow Ag_n \end{gathered}$$

Examination of the Ag surface after a pulse of NO_2 shows a roughened Ag substrate, coated with $AgNO_3$ in which Ag microclusters are imbedded. The **SERS** signal originates from a twofold roughness: one which is large scale on the residual powder surface, and the other on the newly formed Ag clusters. The Ag_n microclusters are also very catalytically reactive. They react preferentially with a second pulse of NO_2, a process which consumes the clusters and diminishes the charge transfer enhancement until new clusters are formed by the auto catalytic decomposition of $AgNO_2$.

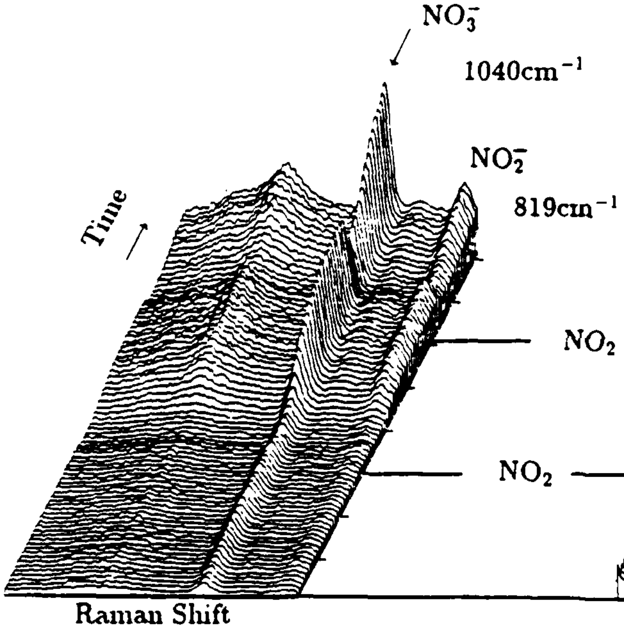
If the amount of gas is relatively small, the heating of the surface will be relatively small, and large scale roughness reconstruction will be negligible. In this case, the EM enhancement will be constant, and the normalized **SERS** intensity will be proportional to the coverage, θ.

If the heat of reaction is large, not only will the adatoms be consumed, but the surface morphology will changed. The adsorbate molecules become mobile and relinquish their role as surface migration inhibitors. As a consequence the kinks, edges and canyons characteristic of large scale roughness will disappear making the surface smoother until the heat is lost. At that point the roughness is reestablished as the adsorbates inhibit mobility.

Figure 3a is the room temperature **SERS** spectra obtained in a sequence of increasing surface reaction heats. Two pulses of NO_2 ($85\mu L$, $\sim 3.5 \times 10^{-2}$ cal/pulse at 1% reaction) were passed over a Ag powder after an initial pulse of NO_2 had prepared the Ag microstructures in $AgNO_3$. Careful examination of the **SERS** signal shows that the background intensity is coordinated with the surface chemical treatment. In fact the background (1000-1500 c/s) mimics the intensity variation of the peaks of the **SERS** signal. Thus the adatom concentration depends on the chemical reaction process.

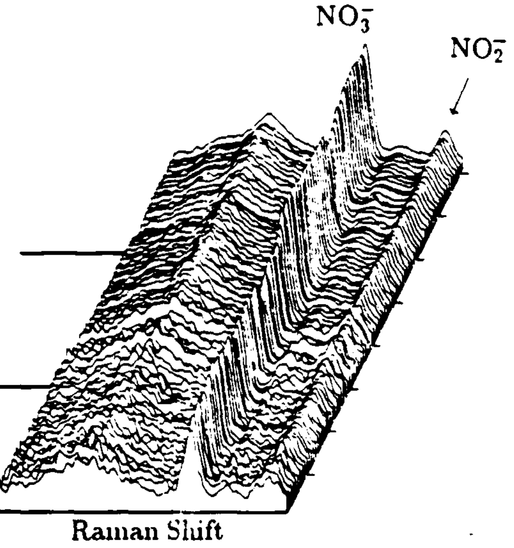
Figure 3b shows the same **SERS** spectra but normalized to the background intensity. The second pulse of NO_2 gas increases the normalized intensity of the peak due to adsorbed NO_3^- by about 25%. The normalized intensity of the NO_2^- peak is constant during the same treatment. A third pulse of NO_2 momentarily decreases the intensity of the normalized NO_3^- peak before it again reaches it previous intensity within 10%.

These results may be explained by assuming that the initial gas pulse reacts with the surface oxide and Ag_2CO_3 to form nitrates and limiting the portion of gas which actually forms the initial nitrite. The second and third pulses of NO_2 show a saturation of the normalized intensity, indicating that the initial pulse produced about 75% complete coverage. The **SERS** data show large changes in intensity at each reaction due to the formation of Ag microstructures which serve as sites for adatom or charge transfer enhancement. While the number of such sites is small after the initial pulse of NO_2, the *second* pulse produces a large increase in the concentration. With the arrival of the third pulse, a large decrease in the **SERS** intensity results because the NO_2 reacts with with the Ag microclusters. However, the normalized intensity curve shows only a 25% drop in intensity in the same time interval indicating that the large scale roughness is also affected. This is not unreasonable since the NO_2 effective concentration is greater in the absence of the scavaging reactions.



SERS

Figure 3a



Normalized **SERS**

Figure 3b

Example III. The third example, which demonstrates that the background intensity is important, is the decomposition of $(CH_3O)_2CH_3PO$, (DMMP), on Ag metal powders which have previously been exposed to air. The Ag_2O layer covers the surface along with carbonates as previously noted. Experiments under UHV conditions using thermal desorption techniques have shown that adsorbed Ag_2O is very basic, and will remove H even from CH_3OH to form the adsorbed methoxy, CH_3O-, and -OH radicals[1]1.

If the **SERS** spectra obtained from the decomposition of DMMP on Ag is examined, a peak at 2924 cm^{-1} is observed, which may be assigned to adsorbed methoxy species. No evidence of adsorbed -OH near 3600 cm^{-1} is found presumeably because extensive hydrogen bonding broadens the **SERS** peak. The two **SERS** peaks at 930 cm^{-1} and 1100 cm^{-1} are evidence for the formation of both $H_2PO_4^-$ and $HPO_4^=$ as products [8,9]. Other fragments may exist on the surface from the decomposition of DMMP but have not been observed.

Figure 4a shows the time evolution of the **SERS** peak at 2924 cm^{-1} due to adsorbed CH_30-. A previous exposure to a pulse of NO_2 gas was used to prepare the Ag microclusters. Subsequently, a series of NO and DMMP vapor pulses, as shown, were passed through the Ag powder to develop the methoxy signal. It is apparent that each NO pulse not only increases the **SERS** peak intensity, but increases the background intensity. The addition of DMMP also increases the signals. By normalizing the **SERS** spectra to the background once more, the resulting spectra due to the coverage of methoxy radical shows little variation after the initial pulse of DMMP vapor has been degraded. This result implies that at room temperature the degradation of DMMP is impeded after about 100s (the time interval between frames is 3.3s) at which time the surface is saturated.

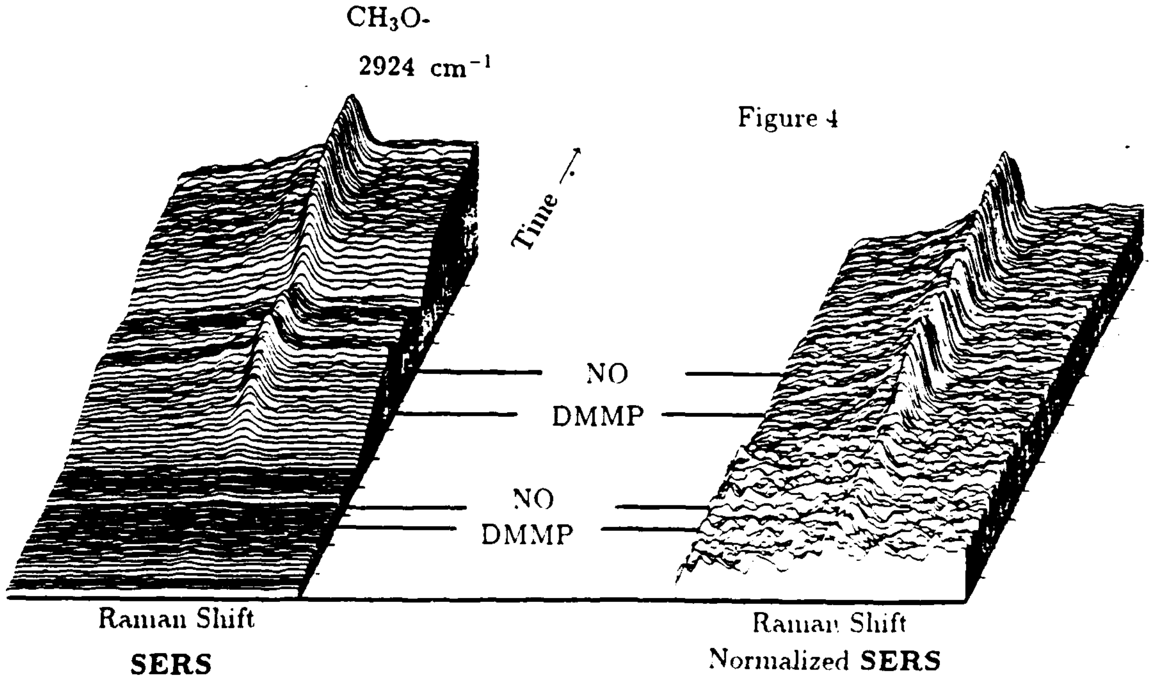


Figure 4

CONCLUSIONS

Three examples of experimental evidence have been provided to show that the time dependence of the intensity of **SERS** spectra obtained from Ag powder subjected to chemical processes may be separated into two distinct contributions: 1) the electromagnetic enhancement and 2) the charge transfer enhancement mechanism. The charge transfer enhancement manifests it contribution not only in the **SERS** peaks intensities, but in the intensity of the background signal. Since the background signal is proportional to the adatom concentration, it may be used to normalize the **SERS** signal to obtain spectra whose intensities are linearily related to the adsorbate coverage providing the reaction heat does not grossly reconstruct the subtrate metal surface.

Other examples which support this method for a measurement proportional to θ are the **SERS** spectra of the formation of adsorbed H_2O in electrochemical systems, the reactions of acetylene and substituted acetylenes with Ag microclusters, the reaction of ethyl and hexyl phosphonates, and the replacement of NO_3^- adsorbed on Ag with $SO_4^=$. This technique will simplify the interpretation of **SERS** spectra providing a means of measuring adsorbate coverages necessary for the analysis of surface catalyzed chemical reaction kinetics.

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