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RAMAN SPECTROSCOPY AS A PROBE OF ADSORPTION ON RHODIUM

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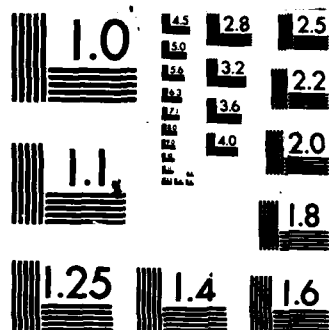
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Raman Spectroscopy as a Probe of Adsorption on Rhodium Particles

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Abstract:

Raman spectroscopy has been used as a probe of the adsorption of pyridine onto small particles of rhodium. The band energies of the surface phase correspond with those found on roughened silver electrodes. Chemical experiments indicate that the pyridine is strongly chemisorbed. The similarity with the spectrum of pyridine on Ag presumably means that the predominant surface species is the same on each metal. This work represents the first report of an enhanced Raman spectrum on metallic rhodium.

Introduction:

Surface enhanced Raman spectroscopy, SERS, has served to renew interest in Raman spectroscopy as a probe of adsorption phenomena. Most workers have focused their attention on adsorption on metals on which the effect is large, e.g. Ag, Au and Cu. Recently, small enhancements have been observed on the Group VIII elements, Pd, Pt, Ni, (1,2,3,4,5,6,7). Since rhodium is one of the most catalytically important of the second row transition elements, chemisorption processes on its surface are of fundamental importance. We wish to report the first enhanced Raman effect on metallic rhodium: that of pyridine on small rhodium particles prepared both as an aqueous colloid and as a supported metal. Simple chemical experiments on the aqueous colloid indicate that the association between the adsorbate and the metal particle is quite robust.

Experimental:

Rhodium colloid samples were prepared in analogy to a published method for a platinum sol (8). A volume of a boiling 5% formaldehyde solution was slowly added to an equal volume of a boiling 5% (weight %) RhCl_3 solution and then allowed to boil for 30 minutes. A dark green sol resulted and after a few minutes a black precipitate formed. The sol was decanted from the precipitate, diluted and a small amount of sodium citrate was added to stabilize it. The resulting stable green sol was then aged for two weeks before Raman spectra were collected. Electron microscopy indicated that the bulk of the colloidal particles were in the 12-20 angstrom range.

The supported rhodium sample was prepared according to the prescription of Yang and Garland (9). The rhodium content was 10% by weight. The aluminum oxide, Linde high purity abrasive (<1 micron), was boiled in a 30% H_2O_2 solution for five hours and then oven-dried before sample preparation. The B.E.T. surface area of the aluminum oxide was $76 \text{ m}^2/\text{gram}$. This corresponds to a rhodium coverage of 0.5-1.0 monolayer. The impregnated alumina was applied to a CaF_2 plate which was then mounted in the UHV cell. Reduction of the rhodium salt occurred under 2 psig of hydrogen, Matheson prepurified grade, at $150\text{--}170^\circ\text{C}$. The cell was then pumped to 5×10^{-7} torr overnight. Pyridine was admitted as a vapor to a total pressure of 40 torr.

The solutions used in the preparation of the colloid in the chemical experiments were all prepared using Millipore conductivity water. The pyridine was freshly distilled before use. The ion exchange resin used was Amberlite MB-1.

The Raman spectrometer was of the conventional type and all spectra were measured relative to the 488.0 nm line of an argon ion laser. The colloid and

solution spectra were measured in sealed capillary tubes. The spectrum of pyridine on supported rhodium was obtained in a specially constructed cell, constructed from a stainless steel 6-way UHV cross fitted with three windows, a gas inlet port, connections to an external sorption pump and an integral 8 l/sec ion pump. The sample itself was mounted on a CaF_2 plate attached to a rotary feedthrough. Raman spectra were obtained using two of the windows and a 45 degree collection angle.

Results and Discussion:

The well documented enhancement of the Raman spectrum of pyridine on silver has led to the use of this adsorbate as a test molecule when examining other metals for evidence of SERS (4,5,7,10,11). In this paper we restrict our results to the Raman spectrum of pyridine in the 1000 cm^{-1} region in which the strongest Raman bands occur.

Figure 1 shows the Raman spectra of pyridine in this region under four different conditions. Spectrum A is the Raman spectrum of aqueous 0.25M pyridine. The two bands observed in this spectrum have been assigned to the symmetric (1004 cm^{-1}) ring breathing modes of pyridine. Spectrum B is that of pyridine plus the aqueous colloid in a solution where the pyridine concentration is the same as that in A. The new band, at 1025 cm^{-1} that is observed has been reported for pyridine on a silver electrode (12). Fleischmann et al. (13) assigned this band to the symmetric breathing mode of a chemisorbed pyridine species and called this species a Lewis acid coordinated pyridine. They attributed the origin of these Lewis acid sites to laser photolysis of electrogenerated silver chloride (13). A simple chemical method of determining if in fact this middle band is a result of chemisorption is to do chemistry on the free pyridine and remove it from

the cell. In spectrum C sulfuric acid was added to convert bulk and weakly bound pyridine to the pyridinium ion. The solution was then passed through an ion exchange column to remove the pyridinium salt. In this process most of the colloid is lost, and the water used to wash the solution down the column serves to dilute the solution even further, making the signal very much weaker. However, the Raman band at 1025 cm^{-1} , assigned to surface phase pyridine, persists and the bulk bands disappear. This result suggests that pyridine is tightly bound to the rhodium colloid since it is not removed by H^+ which could, in principle, compete with acceptor sites on the metal for pyridine. Fleischmann et al. (13,14) made their assignment of the pyridine band at 1025 cm^{-1} by analogy to that observed for ZnPy_2Cl_2 . One might argue that the band seen in C is just the pyridinium salt which passed through the ion exchange column unexchanged. This is of course possible, but in figure 1D, the spectrum of pyridine adsorbed from the gas phase is taken as evidence that the Raman band at 1025 cm^{-1} is due to a surface species and is not due to pyridinium formed as a result of aqueous acid-base chemistry. Spectrum D provides evidence that the chemisorbed pyridine is of the same form regardless of the supporting medium. The similarities in the energies of the ring breathing modes on Ag and Rh would seem to indicate that the geometry of adsorption is the same in each instance. Demuth et al. (15) proposed an absorptive state for pyridine on Ag(111) at $\theta > 0.5\text{L}$ involving predominately silver nitrogen bonding with the pyridine C_2 axis nearly perpendicular to the metal surface and we believe that a similar bonding pattern prevails on rhodium surfaces (16). The signal in this spectrum is much weaker than that in solution, but it has been previously noted that Raman scattering from surfaces in vacuo is much weaker than that from the same species in an aqueous medium (17).

There have been many models proposed to account for the enhanced Raman effect. In some sense these models may be divided into two groups, those in which the enhancement is attributed to an electrodynamic effect, and those in which it is thought to be due to some chemical effect. Since rhodium, unlike silver, does not behave as a free electron metal, a substantial electrodynamic enhancement of the Raman spectrum is not anticipated (18). Nonetheless, a significant signal from chemisorbed pyridine in an aqueous medium is observed. A similar spectrum is observed for pyridine adsorbed from the gas phase onto highly dispersed rhodium. These data give credence to the chemical models of the enhanced Raman effect. Indeed, our experiments indicate that considerable chemical interaction occurs in the adsorption of pyridine on rhodium, since the pyridine is not removed from the surface of the colloid by a strong protic acid. We cannot make any reliable estimates of the magnitude of the enhancement of the Raman signal, except that the signal assigned to the chemisorbed species is comparable in magnitude to that of the 0.25M bulk aqueous pyridine. Our results indicate that, in suitable cases, enhanced Raman effects can be observed on metal colloids and on small metal particles and thin films such as those used in catalytic chemistry. Direct vibrational characterization of adsorbate structure and bonding and possibly of intermediates in catalytic cycles appears feasible.

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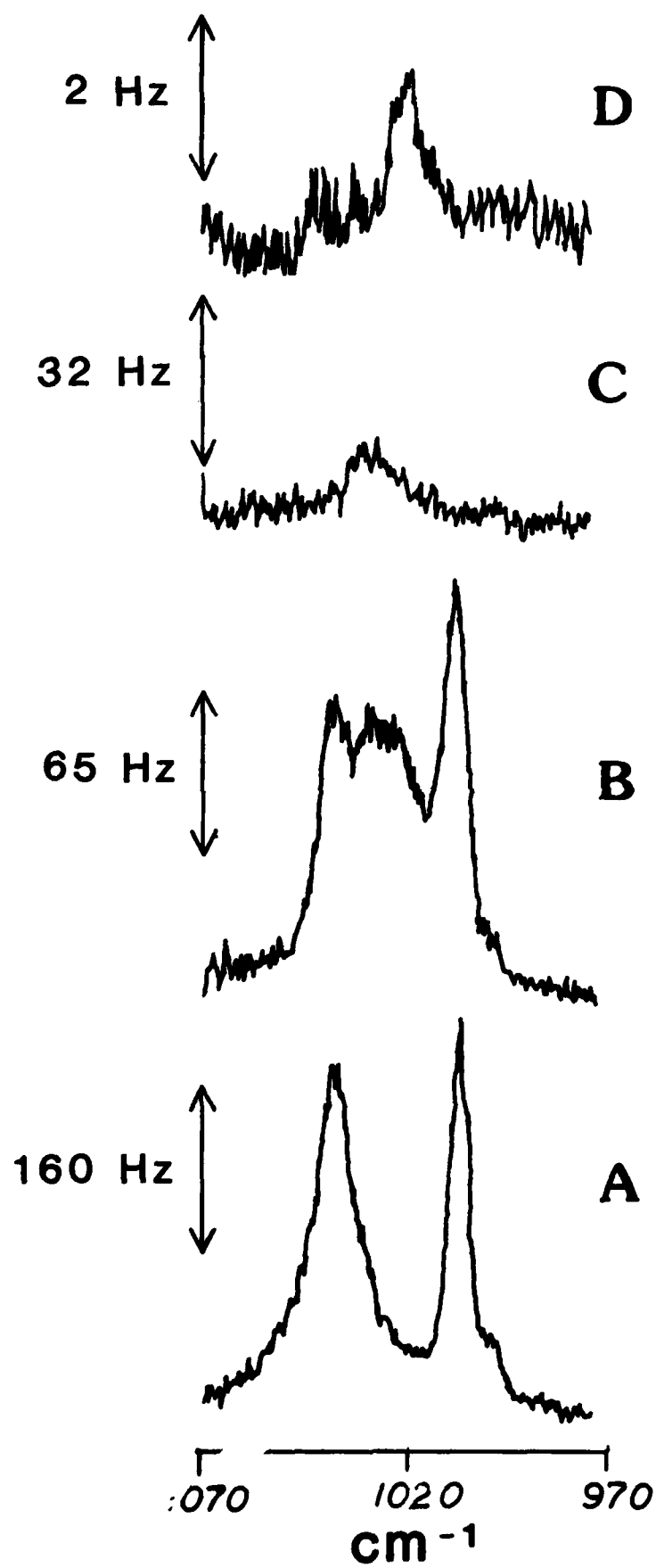
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Figure 1. Raman spectra of pyridine on rhodium A. aqueous pyridine 0.25M. B. pyridine in the aqueous colloid 0.25M pyridine. C. Spectrum obtained when 5 mls of a 10% H_2SO_4 solution is added to 20 mls of the solution which gave spectrum B and then this mixture was passed down an ion exchange column. D. Raman spectrum of pyridine on supported rhodium. 10% by weight on alumina, pyridine pressure was ~40 torr. Laser power 200 mW.



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