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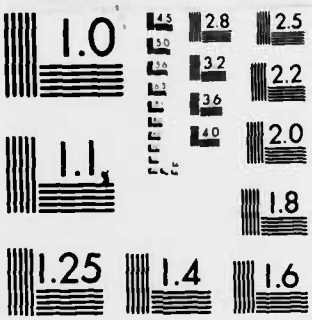

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Observation of Surface-Enhanced Raman Scattering for Transition-Metal Hexaammine Cations at the Outer Helmholtz Plane: Implications for Enhancement Mechanisms at Electrochemical Interfaces

by

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OBSERVATION OF SURFACE-ENHANCED RAMAN SCATTERING FOR TRANSITION-METAL HEXAAMMINE CATIONS AT THE OUTER HELMHOLTZ PLANE: IMPLICATIONS FOR ENHANCEMENT MECHANISMS AT ELECTROCHEMICAL INTERFACES

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The recent observation of surface-enhanced Raman scattering (SERS) for a variety of adsorbates at silver in electrochemical and gas-phase environments has generated a plethora of theoretical models to account for the remarkable (ca. 10^6 fold) observed enhancement of the Raman scattering intensities.[1] These models can be divided into those demanding only the presence of the Raman scatterer at or close to the metal surface ("physical models"), and those requiring specific adsorbate-surface interactions ("chemical models").[1d-g] Prompted in part by the especially intense SERS seen for specifically adsorbed species at silver electrodes, a widely held viewpoint is that the enhancement is due in part to chemical interactions between the Raman scatterer and the metal surface, possibly involving an adsorbate-adatom "complex".[1b-g]

This report examines ~~We have been examining~~ SERS of inorganic adsorbates at silver-aqueous interfaces.[2] One objective is to examine systematically how the SER spectra are influenced by the nature of the adsorbate-surface interactions. A valuable class of adsorbates for this purpose is provided by substitutionally-inert Cr(III), Co(III), Ru(III) and Os(III) amine complexes containing ligands such as thiocyanate, bromide, or pyrazine that bind strongly to silver electrodes.[2b,2d-f,3] The nature of the adsorbate-surface interactions can be systematically altered by varying this bridging ligand. In addition, the surface concentrations are readily obtained from the charge required to reduce the metal cation.[3]

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A general feature of their SER spectra is the appearance of metal-ammine and internal ammine modes as well as bands associated with the surface-bound ligands.[2d-f] The ammine modes are easily identified from the diagnostic frequency shifts that occur upon deuteration of the ammine hydrogens.[2e,4] Either 0.1 or 0.01 M KCl, or 0.05 M KBr was used as the supporting electrolyte along with 0.05-1 mM of the ammine complexes. The silver electrode was roughened by means of an oxidation-reduction cycle. Raman excitation at 647 nm was used to avoid ammine photodecomposition. Further experimental details are given elsewhere.[2a,d-f]

An unexpected finding was the observation of a metal-ammine stretching mode (ν_{M-N}, ca. 450 cm^{-1}) for $Cr(NH_3)_5F^{2+}$ and $Cr(NH_3)_5NO_3^{2+}$ although neither fluoride nor nitrate anions are significantly adsorbed at silver in the presence of chloride.[2b,5] These results prompted us to examine SERS of $Cr(NH_3)_6^{3+}$. Indeed, a chromium-ammine stretching mode of comparable intensity to that seen for the surface-attached ammines was obtained, even though $Cr(NH_3)_6^{3+}$ clearly lacks a means of binding to the silver surface. The frequency of this band, 450 cm^{-1}, is close to that for the A_{1g} mode in the normal Raman spectrum.[6]

Representative SER spectra obtained for adsorbed $Cr(NH_3)_5NCS^{2+}$, $Cr(NH_3)_5Br^{2+}$, and $Cr(NH_3)_6^{3+}$ are shown in Fig. 1. The first two complexes are known to be adsorbed in amounts approaching a monolayer (2×10^{-10} mol cm^{-2}).[3] Extensive surface binding is confirmed by the appearance of sulfur- and bromide-surface modes, ($\nu_{Ag-S} \approx 220$ cm^{-1}, $\nu_{Ag-Br} \approx 160$ cm^{-1}) in the SER spectra of $Cr(NH_3)_5NCS^{2+}$ and $Cr(NH_3)_5Br^{2+}$ obtained in KCl (Fig. 1C,D). Note that the ν_{M-N} mode for $Cr(NH_3)_6^{3+}$ at 450 cm^{-1} has a roughly comparable intensity to that for these surface-bound complexes. [The comparison of $Cr(NH_3)_5NCS^{2+}$ with $Cr(NH_3)_6^{3+}$ is expedited by deuterating the ammine ligands (dashed curves) in order to remove the accidental degeneracy of the δ_{NCS} and ν_{Cr-N}

modes (Fig. 1B,D)]. Peaks are also seen at 265 cm^{-1} and 160 cm^{-1} in chloride and bromide electrolytes (Fig. 1A,B), ascribed to ν_{Ag-Cl} and ν_{Ag-Br}.

Comparable results were obtained for $Co(NH_3)_6^{3+}$, $Ru(NH_3)_6^{3+}$, and $Os(NH_3)_6^{3+}$. Symmetric N-H stretching modes at ca. 3200 cm^{-1} were also observed in each case. For $Co(NH_3)_6^{3+}$, peaks at both 515 and 450 cm^{-1} were seen, consistent with the A_{1g} and E_g vibrational modes in the bulk-phase Raman spectrum.[8,9] Examination of $Ru(NH_3)_6^{3+}$ is of particular interest since this undergoes reversible reduction to $Ru(NH_3)_6^{2+}$ (formal potential E_f^b = -180 mV vs. s.c.e.[10]). Indeed, altering the potential to more negative values in the region -200 to -400 mV vs s.c.e. yields a progressive replacement of the band at 500 cm^{-1} by one at 460 cm^{-1}. These bands are consistent with A_{1g} Ru^{III}-NH_3 and Ru^{II}-NH_3 vibrations on the basis of the bulk-phase Raman spectra.[4a] The intensity-potential dependencies of these two bands were entirely reversible and quantitatively consistent with that expected for a one-electron redox couple. Thus fitting these data to the Nernst equation yielded a number of electrons, n = 1.0 $\pm$ 0.1, and a formal potential E_f^s = -300 $\pm$ 10 mV vs s.c.e. for 0.05 m$\underline{M}$ $Ru(NH_3)_6^{3+/2+}$ in 0.1 $\underline{M}$ KCl.

The difference between the surface and bulk-phase formal potentials for $Ru(NH_3)_6^{3+/2+}$, $(E_f^s - E_f^b)$, equals the potential ϕ_R at the site occupied by the complex, ϕ_R = (- 300 + 180) = -120 mV. This potential is compatible with that expected at the outer Helmholtz plane (o.H.p.), indicating that the cations are indeed located outside the adsorbed halide layer.[11] Such negative values of ϕ_R also produce extremely large hexaammine concentrations at the o.H.p. Indeed, we have detected diffuse-layer adsorption of $Ru(NH_3)_6^{3+}$ using rapid scan cyclic voltammetry; surface concentrations around 4 x 10^{-11} mol cm^{-2} were determined for 0.05 m$\underline{M}$ $Ru(NH_3)_6^{3+}$ [1g]. These measurements also yield a value of E_f^s for $Ru(NH_3)_6^{3+/2+}$ equal to -290 ± 10 mV. vs. s.c.e.

The foregoing provides persuasive evidence that efficient electrochemical SERS can occur for suitably high interfacial concentrations of unbound molecules even when separated several Angstroms from the metal surface. Moreover, surface attachment seems to yield little or no additional signal enhancement. This is not to deny the importance of adsorbate-surface binding to SERS; clearly specific adsorption will normally be required in order to yield suitably large surface concentrations. Indeed, the intense stable SERS seen for specifically adsorbed anions require coverages approaching a monolayer, apparently due to the stabilization of SERS-active surface morphologies by surrounding close-packed adsorbate.[3b,c] The present results do not contradict this in that altering the potential to more negative potentials where the anion coverage falls below a monolayer leads to irreversible decreases in the SERS signal for the hexaammine as well as for the adsorbed anion. Thus the sites stabilized by the *surface-bound* halide ions also appear to provide SERS for *unbound* hexaammine cations.

The present results therefore call into question SERS models requiring chemisorption of the Raman scatterer to the metal surface. Nevertheless, "surface resonance" enhancement mechanisms involving photon-induced charge transfer between the metal surface and the Raman scattering molecule[1b-g] are not necessarily precluded on the basis of these data since efficient electron tunneling is known to occur between metal surfaces and cations at the o.H.p.[12] However, it is unclear to what extent such charge-transfer models require chemisorption of the Raman scatterer in order to align the energies of the Fermi level and adsorbate electronic states.[1e-g] Further theoretical work should clarify this situation.

Acknowledgments

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(11) Given that there is close to a monolayer of bromide or chloride anions present under these conditions,[2b] the potential at the o.H.p. is calculated from Gouy-Chapman theory to be around -100 mV.

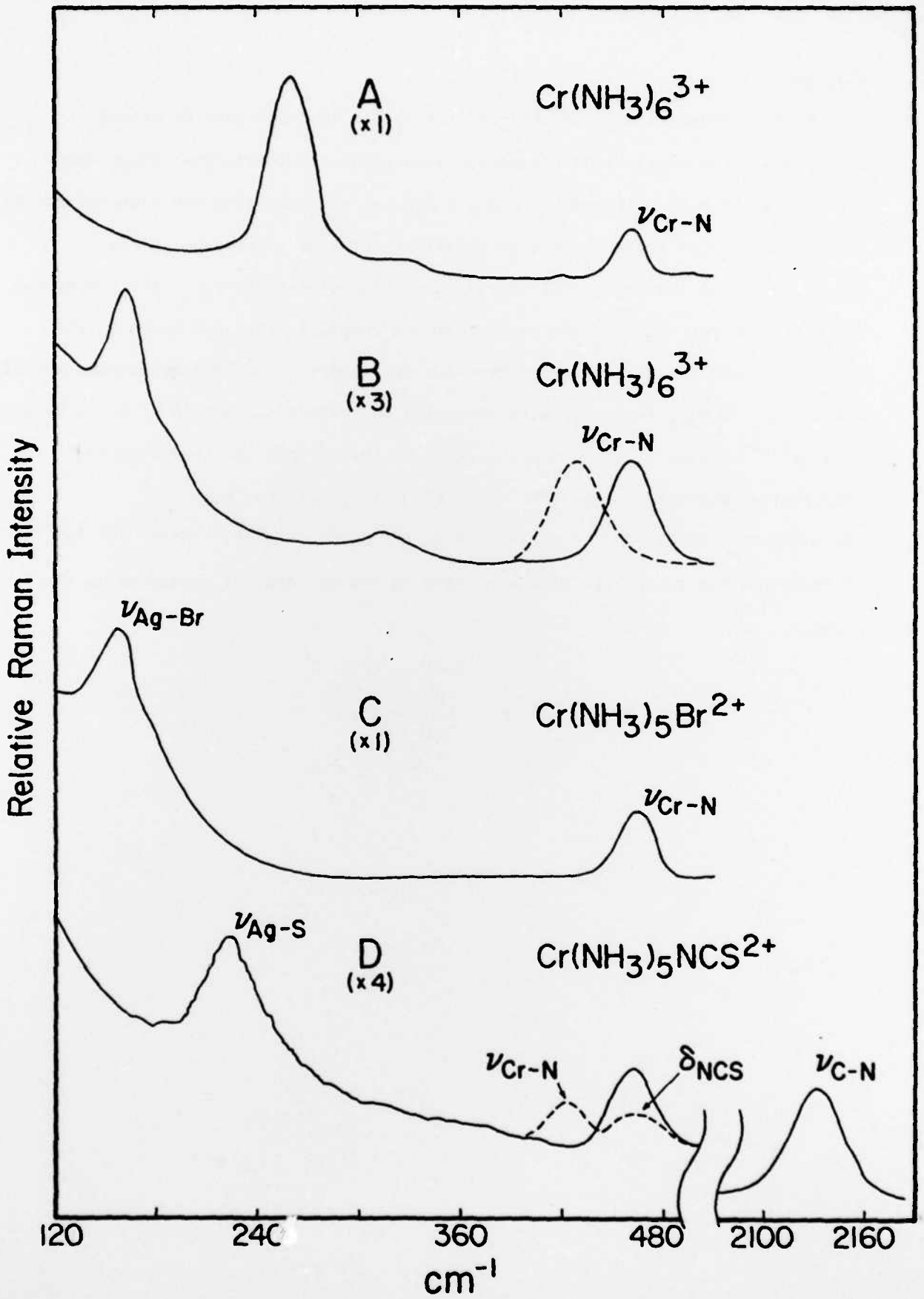
(12) J.T. Hupp, M.J. Weaver, J. Electroanal. Chem., 152, 1 (1983), J. Phys. Chem., in press.

Figure Caption

SER spectra for Cr(III) ammine complexes at silver-aqueous interface in 120-500 cm^{-1} region. (A) 1 m$\underline{M}$ $Cr(NH_3)_6^{3+}$ in 0.01 $\underline{M}$ KCl, -300 mV vs. s.c.e. (B) 1 m$\underline{M}$ $Cr(NH_3)_6^{3+}$ in 0.05 $\underline{M}$ KBr, -200 mV. (C) 1 m$\underline{M}$ $Cr(NH_3)_5Br^{2+}$ in 0.01 $\underline{M}$ KCl, -100 mV. (D) 1 m$\underline{M}$ $Cr(NH_3)_5NCS^{2+}$ in 0.01 $\underline{M}$ KCl, -100 mV. Dashed curves for B and D denote spectral segments obtained for corresponding deuterated ammine. Spectrum (D) also includes ν_{C-N} mode (2130 cm^{-1}). Spectra obtained using ca. 100 mW of 647 nm laser irradiation.

Abstract

Surface-Enhanced Raman Scattering (SERS) has been observed at silver electrodes for several transition-metal hexaammine complexes even though these cations cannot bind to the metal surface and are excluded from the electrochemical inner layer by the presence of a monolayer of chloride or bromide anions. The intensity of the SERS metal-ammine stretching vibrations ν_{M-N} are comparable to those seen for closely related pentaammine complexes that are bound to the surface via specifically adsorbed coordinated ligands. For hexaammineruthenium(III), changes in the ν_{M-N} frequency with potential indicate the presence of an interfacial $Ru(NH_3)_6^{3+/2+}$ couple. The formal potential of this couple obtained from the potential dependence of the SERS intensities is consistent with the Raman scattering ions being located at the outer Helmholtz plane. The implications of these results to current models of SERS in electrochemical environments are noted.


A
(x 1)
$Cr(NH_3)_6^{3+}$
ν_{Cr-N}
B
(x 3)
$Cr(NH_3)_6^{3+}$
ν_{Cr-N}
ν_{Ag-Br}
C
(x 1)
$Cr(NH_3)_5Br^{2+}$
ν_{Cr-N}
ν_{Ag-S}
D
(x 4)
$Cr(NH_3)_5NCS^{2+}$
ν_{Cr-N}
δ_{NCS}
ν_{C-N}
Relative Raman Intensity
120
240
360
480
2100
2160
cm^{-1}

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