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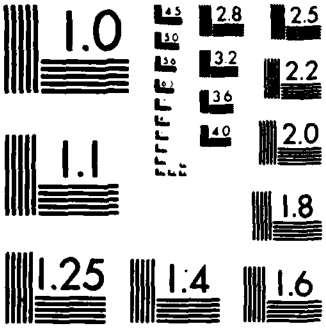

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER
Technical Report No. 5

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)*
The Interpretation of Very Low Frequency Raman Scattering from Roughened Silver Electrodes: Clusters, Cavities or Complexes?

5. TYPE OF REPORT & PERIOD COVERED
Technical

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
Robert M. Corn and Michael R. Philpott

8. CONTRACT OR GRANT NUMBER(s)
N00014-82-C0583

9. PERFORMING ORGANIZATION NAME AND ADDRESS
IBM Research Laboratory, K33/281
5600 Cottle Road
San Jose, CA 95193

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

12. REPORT DATE
July 1984

13. NUMBER OF PAGES
12 + 3 figures

14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*

15. SECURITY CLASS. *(of this report)*
UNCLASSIFIED

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*
Approved for public release; distribution unlimited.

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JUL 27 1984
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17. DISTRIBUTION ST ENT *(of abstract entered in Block 20, if different from Report)*
Approved for public release; distribution unlimited.

18. SUPPLEMENTARY TES
Prepared for publication in Journal of Chemical Physics

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*
Raman Scattering
Surface
Enhanced
Electrodes, Silver

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

84 07 25 008

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by

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Prepared for Publication

in

Journal of Chemical Physics
(1984)

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ABSTRACT: The potential dependence of the broad low frequency (5-8 cm^{-1}) Raman scattering features from roughened silver electrodes and their sensitivity to the chemical composition of the supporting electrolyte are presented. We find that the electromagnetic enhancement theories which relate these Raman bands to the vibrations of the silver surface structures are unable to account for all of the data; electronic coupling to the stabilizing adsorbates requires that some of the charge transfer concepts of the adatom complex theories be included in the model.

I. INTRODUCTION

Surface roughness has been recognized from the first to be a key factor in the light scattering process from electrochemical systems.[1] An oxidation-reduction cycle (ORC) is required in all but a few instances to see "surface enhancement effects" in surface enhanced Raman scattering (SERS),[2] second harmonic generation[3] and Rayleigh scattering[4] from electrodes. A crucial question which immediately arises when discussing surface roughness is the length scale involved in the surface enhancement. Two roughness scales have been proposed to explain the surface enhancement: atomic scale and large scale or geometric (>50 nm) roughness. In the latter, classical electromagnetic equations show how surface roughness allows the incoming light to couple to the localized surface plasmon modes of the metal, giving rise to an enhancement in the available electromagnetic field amplitude at the surface on the order of 10-100.[5] Experiments with attenuated total reflection (ATR),[6] gratings,[7] colloids,[8] and microlithographic structures[9] verify that at least part of the enhancement of light scattering from surfaces with predesigned topologies is due to these large scale features. By implication it is assumed that similar effects operate at the surface of electrodes roughened by an ORC.

There are, however, several observations for electrochemical systems which the electric field enhancement mechanisms fail to explain. In particular, the SERS signal is lost irreversibly when the electrode is cathodically polarized.[10] Moreover, the intensities of various Raman bands can vary significantly as a function of potential and laser wavelength.[11] To explain these effects a second, atomic scale roughness has been proposed.[2] Adatom complexes on the surface which strongly couple to the molecular adsorbates electronically (and therefore chemically) are postulated to be involved in the

SERS active site.[2] This adatom model has the implicit assumption that the SERS activity is due to a small subpopulation of molecules on the surface. This assumption has been supported by the destruction of the SERS signal by the deposition of a submonolayer (<3%) of lead or thallium atoms on the silver surface.[12,13] The fact that only a small percentage of the surface molecules contribute to the Raman signal implies that perhaps both the geometric and atomic roughness enhancements are necessary to observe SERS signals.

The recently proposed "cavity site" model[14,15] presents the possibility of combining both of these effects into a single picture of the surface morphology. In the thermal desorption studies in UHV evidence is cited which suggests that the some of the pyridine molecules adsorbed on coldly deposited silver films are transported in low temperature annealing processes to the cracks or cavities which occur at the grain boundaries or other defect-like regions. These cavity sites could show enhanced Raman signals from both electromagnetic effects and strong chemical bonding due to the large anisotropy of the cavity size. It is conceivable that similar surface structures could exist in the aqueous electrochemical systems as a result of the activating ORC.[15]

In electrochemical systems the best evidence for some type of surface species or cluster has been obtained by Weitz *et. al.*[16] They observed a broad and inhomogeneous Raman band at very low frequency which they labelled an "inelastic Mie scattering" mode, attributing this band to the antisymmetric breathing vibration of large silver clusters formed at the surface of the electrode during anodization. The observed frequencies (5-10 cm^{-1}) imply a silver cluster size of about 10 nm in diameter, which is on the low end of the geometric roughness scale mentioned previously. An electromagnetic field enhancement for the clusters was cast in the form of a coincidental matching of the laser frequency and the localized plasmon mode, and this enhancement mechanism was used to explain dependence of the band position on the laser excitation frequency. In addition to the inelastic Mie scattering, Weitz *et al.*[16] also reported an additional contribution to the low frequency Raman band which they labelled "inelastic Rayleigh scattering" from the molecules coupled to these low frequency cluster vibrations. This last component was found to be very sensitive to the chemical composition of the electrolyte, and was particularly large in the presence of pyridine.

We have critically examined the sensitivity of these low frequency Raman bands (which for lack of a better name we shall refer to as cluster bands) to the potential of the silver electrode and to the chemical composition of the electrolyte. The cluster bands have a potential dependence similar (but not identical) to the molecular SERS bands which have been observed. The Raman signal is irreversibly lost as the potential is swept negatively towards the point of hydrogen evolution, but there is also a quasi-reversible increase in the band intensity with the same potential change. In addition, we observe an increase in the signal if a small amount of hydrogen is evolved from the electrode prior to the ORC. This fact and the observation that the cluster bands are critically sensitive to the electrolyte employed – but only when that electrolyte is present during the ORC – lead us to conclude that the cluster bands of these roughened electrodes are due to some unusual surface structure which is stabilized by the adsorbates and ligands from the solution. This strong interaction between ligand and silver atom implies that the notions from the adatom model of charge transfer and electronic reorganization of these large metal-ligand complexes must be included in our picture of these surface species.

II. Experimental Considerations

All solutions were prepared from deionized water, reagent grade postassium bromide or sodium chloride, and spectrophotometric grade pyridine. The solutions were deaerated with Ar prior to electrochemical use. A PAR 173 potentiostat and and PAR 175 programmer were used to control a standard three electrode potentiostat which had a Pt wire counter electrode and a Ag/AgCl reference electrode; all potentials stated here are *versus* Ag/AgCl.

The working electrode in the potentiostat was a roughened solid silver electrode which was polished with 0.5 micron alumina, rinsed with deionized water, and inserted into the electrochemical system. The electrode was then roughened by an ORC consisting of a potential step from −400 mV to +200 mV and back again. The time spent at +200 mV was adjusted so that a charge density of 25 mC/cm^2 was delivered to the electrode.

The beam from a Coherent Model 3000-K Kr$^+$ laser was focused onto the roughened electrode with an incident angle of 45 degrees, and the Raman scattering was collected normal the the silver surface. The Raman spectra were obtained by a Spex 14018 double monochromator in tandem with a third grating stage (also supplied by Spex) which provided the necessary stray light rejection. The resolution was set at 0.1 cm^{-1} for recording spectra, and was opened to a 0.5 cm^{-1} bandwidth for the potential dependence studies.

III. RESULTS AND DISCUSSION

A. Cathodic Polarization of the Electrode

Polarization of a roughened silver electrode to a sufficiently negative potential irreversibly destroys the molecular SERS signal.[10,17] However, a large enhancement of the signal is observed in the same systems if hydrogen is evolved at the electrode prior to an ORC.[18] We observe the same effects in the cluster bands. Curve (a) in Figure 1 shows the low frequency Raman spectrum of a silver electrode in a 0.1M KBr+0.02M pyridine solution (an electrolyte comparable to those employed in the previous study[16]) which has been roughened with a mild ORC (25 mC/cm^2) after 10 sec at −1400 eV. An additional cathodic polarization for 5 sec at the same potential destroyed the signal irreversibly as witnessed in a subsequent spectrum (curve (c) of Figure 1). The ability to enhance or destroy the Raman signal reaffirms the belief that the bands are due to some volatile surface species, whether it be a metal cluster, cavity site, or adatom complex. The irreversible loss of the surface species in the electrochemical systems is most likely a two step process: desorption of the stabilizing ligands/adsorbates followed by the dissolution or reorganization of the silver surface structure. The effect of hydrogen evolution prior to the ORC has been described as "cleansing";[18] this word is quite meaningful in the context of cavities and crevices.

B. The Effect of the Chemical Composition of the Electrolyte

The assumption that the surface species responsible for the cluster band are energetically unstable structures formed during the ORC is supported by the band's sensitivity to the particular solution employed as an electrolyte. We observe that the intensity of the cluster band is larger in a 0.1M KBr+0.02M pyridine solution than in a 0.1M KBr solution, which in turn is larger than the signal from a 0.1M KCl electrolyte (in which the band is barely visible). More importantly, we find that the addition of pyridine to the 0.1M KBr solution does not increase the intensity of the cluster band; the enhancement is observed only upon reanodization of the roughened silver electrode. The same is true for the addition of bromide to a 0.1M chloride solution: no intensity increases are observed until the electrode is subjected to another ORC. These results are in sharp contrast to the molecular SERS spectra. In the bromide/chloride system, the Ag-Cl stretching band at 240 cm^{-1} is replaced by a Ag-Br stretching band at 190 cm^{-1} upon the addition of bromide to a 0.1M chloride electrolyte.[18] This displacement agrees with differential capacitance studies[19] which show that bromide is much more strongly adsorbed to a silver electrode than chloride ions.

The inability to chemically alter the Raman signal suggests that the chemical enhancement of the signal comes primarily from the particular molecule's (or ion's) role in the production/stabilization of the surface species. The fact that the signal does not change also means that the ligands involved in the surface species are behaving differently than the bulk surface ligands, *i.e.*, there is strong chemical interaction and bonding occurring at the surface structure ligand sites. In terms of the adatom complex model this interaction allows for possibility of charge transfer processes and resonant effects.

As a final note we mention in passing that laser irradiation effects during the ORC appear to make a small contribution to the enhancement of the production of surface structures, but they were not examined in detail here.

C. The Bandshape of the Cluster Band

One of the most intriguing observations made by Weitz *et. al.* was that the position of the Raman cluster band shifted with the laser excitation wavelength. This shift is seen in curve (b) of Figure 1, which was taken with the 647.1 nm line of the Kr^+ laser. Weitz *et. al.* attributed the shift to the selection (by the laser) of the localized plasmon frequency of a different subpopulation of metal clusters present on the electrode (presumably similar plasmon matching conditions could be obtained from the surface cavity sites). Their interpretation implies that a change in bandshape with potential, if observed, would mean the selective dissolution of certain metal clusters.[20] We found no change in the bandshape as a function of potential for the systems we examined. However, Genack *et al.*,[21] in an earlier paper, did see a potential dependent bandshape from a solution of pyrazine.

An alternative explanation for the shift in frequency is to allow for a large distribution of charge transfer complexes which one tunes through as the laser frequency is changed. The Raman signal is then due to this distribution of silver cluster types, each subpopulation having their own charge transfer bands and electronic-vibrational coupling terms. Such a picture would also give a large inhomogeneous bandshape that depended on the laser wavelength.

D. The Potential Dependence of the Cluster Band

In addition to the irreversible changes in the cluster band's intensity there is a quasi-reversible intensity dependence on the potential of the silver electrode. This quasi-reversible behavior can be decoupled from the irreversible loss of signal by monitoring the intensity of the band while cyclically ramping the electrode potential. The results for the cluster band at 8 cm^{-1} with the 530.9 nm laser line are graphed in

Figure 2a. Each time the potential is swept negatively there is some irreversible loss of the signal; this loss is monitored by the decrease in the signal at a particular potential as a function of the number of cycles. Added to this irreversible signal loss is a reversible increase in the band's intensity. This increase is most easily explained in terms of a change with potential in the silver-adsorbate bonding. In the language of the adatom complex model one would consider this signal change as due to the shifts in the various charge transfer levels of the complex.

The potential dependence of the cluster band at 5 cm^{-1} with a laser excitation frequency of 647.1 nm is shown in Figure 2b. The signal is lost irreversibly at a slightly faster rate than the signal with laser light at 530.9 nm (the potential dependence off the peak at 5 instead of 8 cm^{-1} with the 530.9 nm line is the same as that shown in Figure 2a). This discrepancy is probably due to laser-induced photochemical effects similar to those mentioned above.

For comparison with the cluster band's potential dependence we have measured the potential dependence of the molecular pyridine band at 1008 cm^{-1} using the same two laser lines (530.9 nm and 647.1 nm). The results are depicted in Figure 3. Striking differences in the reversible and irreversible behavior are observed with the 530.9 nm laser wavelength curves, again indicating that there are significant changes in the adsorbate bonding occurring with the change in electrode potential.

IV. CONCLUSION

From our experiments we can make some delineating statements as to the nature of the cluster band. First, the presence of a broad, inhomogeneous band at very low frequencies suggests that there is a distribution of surface structures, involving many silver atoms and ligands, which is responsible for the signal. Whether these structures should be thought of as spheroidal clusters, cavities or dendrites is still subject to debate. It is clear, however, that these structures are not responsible for all of the SERS signal from these roughened electrodes. The disappearance of the Ag-Cl stretch and the subsequent appearance of the Ag-Br stretch in the absence of any change in the cluster band signal leads us to conclude that the existence of SERS active sites is not intimately tied to the existence of these surface species, which are specific surface structures created during the ORC. The effect of molecules and/or ions from solution on the cluster band intensity is crucial if not completely dominant. However, these chemical effects are mainly the stabilization of the clusters during the ORC. The surface species giving rise to the signal in these electrochemical systems must be thought of containing significant amount of interaction between the silver atoms and the adsorbed ligands. This statement is supported by the changes with potential of the intensities of the various molecular and cluster SERS bands. Therefore, the concepts of the adatom model must be incorporated into our picture of these surface species to completely explain the observed volatility of the Raman signal.

In conclusion the authors would like to acknowledge helpful discussions with D. Weitz, H. Seki, K. Bunding, and J. Gordon II. This work was supported in part by the Office of Naval Research.

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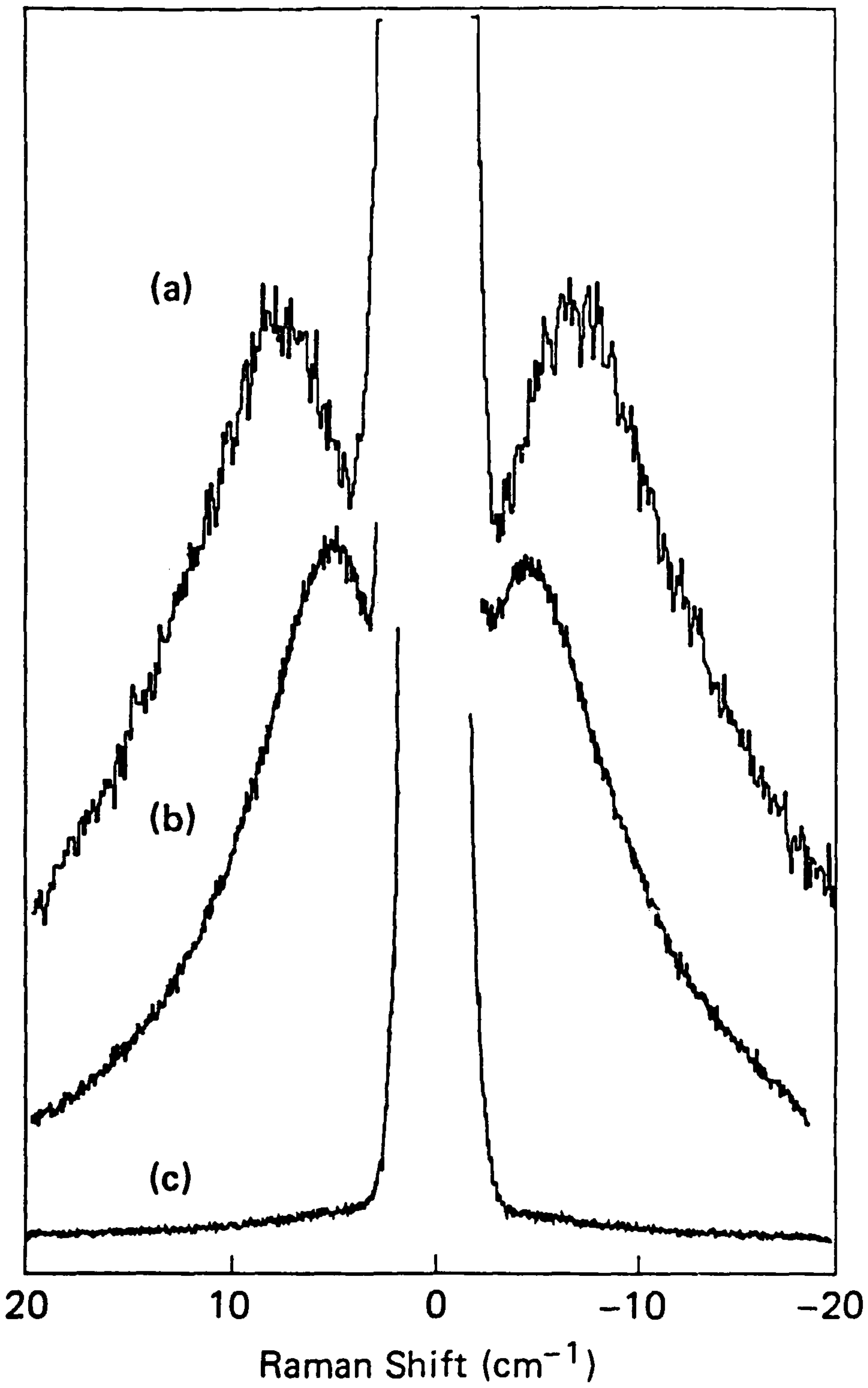
FIGURE CAPTIONS

Figure 1. Low frequency inelastic light scattering from a roughened silver electrode in a 0.1M KBr+0.02M pyridine electrolyte. Incident laser power: 20 mW; resolution: 0.1 cm^{-1}; electrode potential: −400 mV *versus* Ag/AgCl. Curve (a): Stokes and anti-Stokes Raman scattering after the electrode was polarized to −1400 mV for 10 sec and then subjected to an ORC which delivered 25 mC/cm^2 to the electrode; laser wavelength: 530.9 nm. Curve (b): same as curve (a) except with a laser wavelength of 647.1 nm. Curve (c): same as curve (a) except that the electrode potential was held at −1400 mV for 5 sec after the ORC.

Figure 2. Irreversible and reversible potential dependence of the low frequency Raman bands following an ORC. Same electrochemical system as in Figure 1. The potential is ramped cyclically from −400 mV to −800 mV *versus* Ag/AgCl, starting from the end of the ORC at t=0. There is a quasi-reversible increase of the band intensity with increasingly negative potentials coupled to the irreversible loss of the signal in the same potential range. Spectrometer bandwidth, 0.5 cm^{-1}. (a) Laser wavelength, 530.9 nm; (b) Laser wavelength, 647.1 nm.

Figure 3. Irreversible and reversible potential dependence of the 1008 cm^{-1} ring breathing mode of pyridine. Spectrometer bandwidth: 5 cm^{-1}; (a) laser wavelength, 530.9 nm; (b) laser wavelength, 647.1 nm. See Figure 2 caption for details of the electrochemical system.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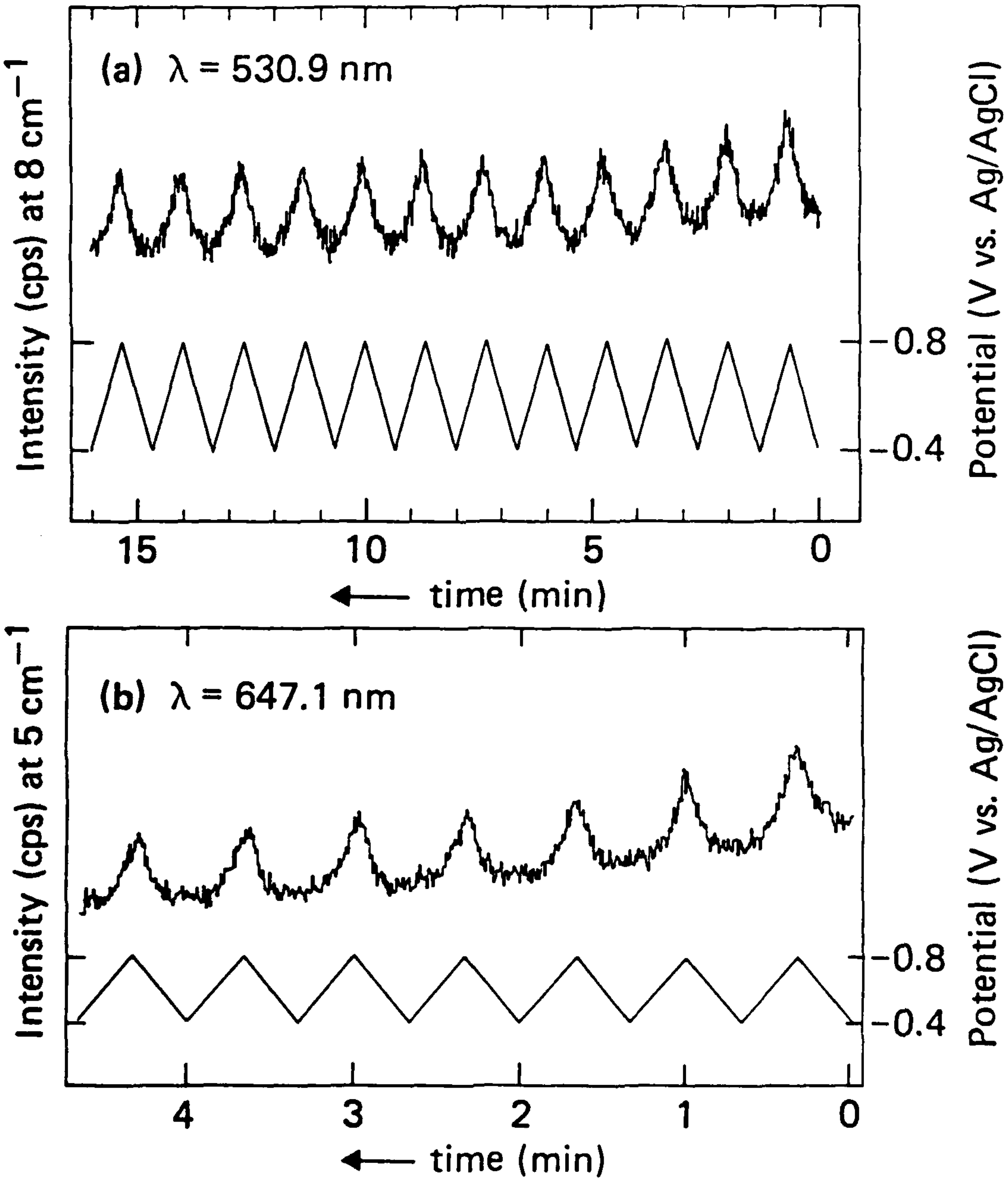
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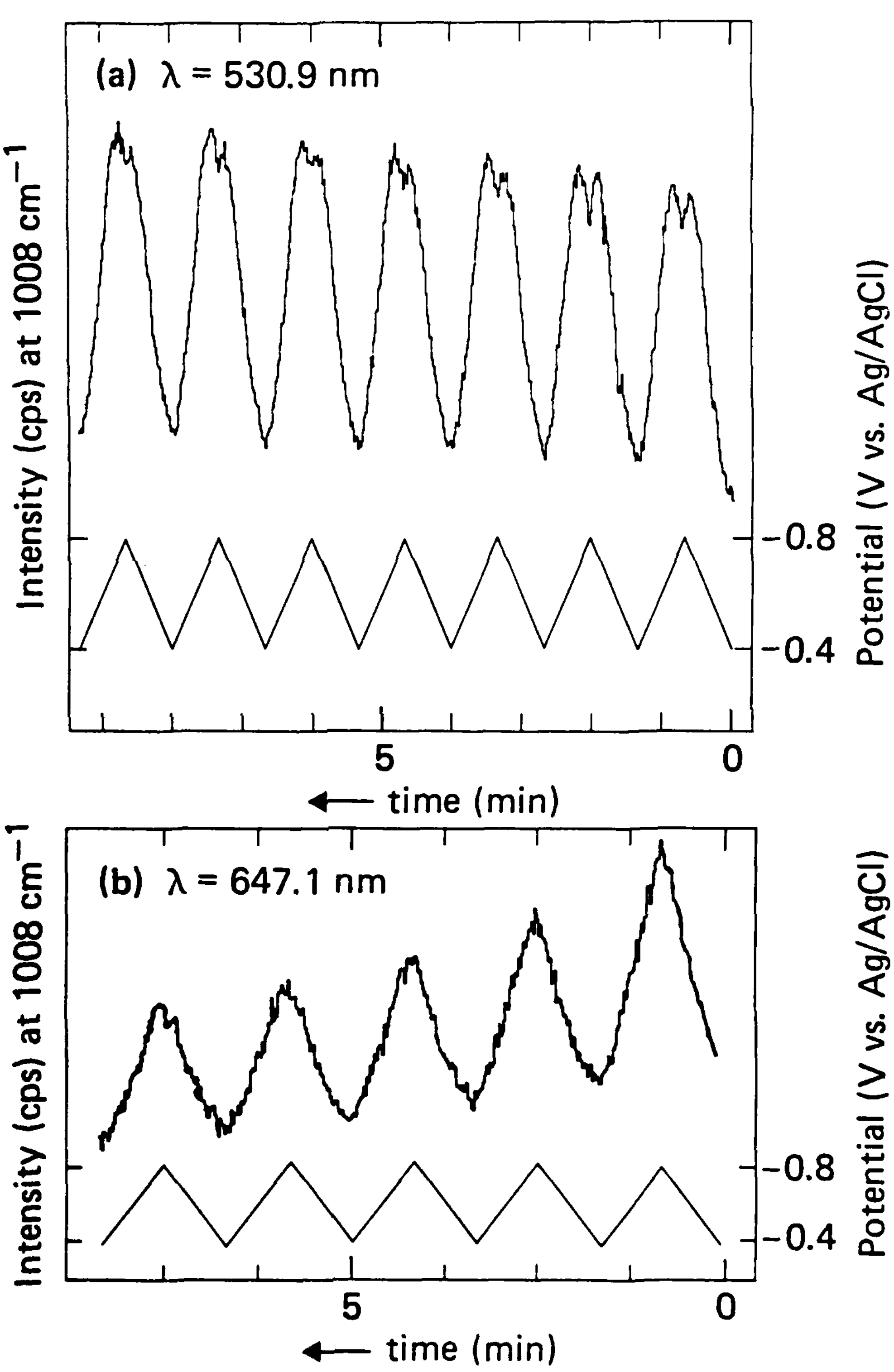
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