THE INFRARED SPECTRA OF SURFACE METAL ATOM VIBRATIONS

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The Infrared Spectra of Surface Metal Atom Vibrations.
SNIFTIRS Studies in the Far Infrared Region using
Time Resolved FTIR Techniques

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The infrared spectra of surface metal atom vibrations. SNIFTIRS studies in the far infrared region using time resolved FTIR techniques.

**Abstract:**
IR spectra of metal atoms on electrodes is discussed.
Short communication

THE INFRARED SPECTRA OF SURFACE METAL ATOM VIBRATIONS

SNIFTIRS STUDIES IN THE FAR INFRARED REGION USING TIME RESOLVED FTIR TECHNIQUES

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Studies of the vibrations of pure metals have historically been pursued by inelastic neutron scattering (which is sensitive to vibrations of the bulk crystal) and more recently by high-resolution electron energy loss spectroscopy, HREELS (which is more sensitive to vibrations of the metal surface). Direct infrared absorbance techniques provide advantages over both of these methods, since they may be used in more hostile environments (such as at the interface between metal and chemical solutions). They have rarely been applied with much success, however, because of the very effective shielding of the electromagnetic radiation by the metal conduction electrons. This results in an exponential damping of the radiation field as it enters the metal phase, with typical skin depths (1/e damping distances) of only a few tens of nm. This damping improves the sensitivity of infrared absorption measurements to the surface vibrations as opposed to bulk phonons, but limits the magnitude of the absorbance considerably. In this report we demonstrate that reflection infrared vibrational spectroscopy may be used to observe the vibrational structure of metallic species deposited on a metal surface which is under electrochemical control.

The surface FTIR spectroscopic technique SNIFTIRS [1] has been shown to be useful for the observation of the vibrational structure of monolayer (or less) quantities of materials adsorbed at the surface of metal electrodes while under electrochemical control. We have now extended the method by modifying the cell and detector design to permit observations in the far infrared region, even below 100 cm⁻¹. In addition, a signal/timer/controller/sequencer and associated software has been developed to allow time resolved infrared spectral measurements to be recorded with 10 μs resolution [2].

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Underpotential, solid solution, alloy formation, and bulk metal deposition studies were made for lithium deposited on gold from acetonitrile solution. At potentials between $-2.40$ and $-2.60$ V, lithium adatoms are underpotentially deposited on a polycrystalline gold surface where they are oxidized rapidly by trace water to solid lithium hydroxide. Between $-2.60$ and $-2.80$ V, this insulating precipitate is reduced to lithium atoms in solid solution with gold, and between $-2.80$ and $-3.10$ V a chemically resistant gold + lithium alloy is formed. At potentials more negative than $-3.10$ V, bulk lithium is formed and reduction of solvent proceeds spontaneously.

Figure 1 shows the SNIFTIRS difference spectrum in a region where one would expect to observe the gold–gold fundamental stretch. Diatomic gold has a vibration frequency of $190.9$ cm$^{-1}$, with a reduced mass of $98.5$ amu [3]. If the gold atom were vibrating with the same force constant against an infinite mass the reduced mass would by $197$ amu, and a vibrational frequency of $135$ cm$^{-1}$ would be expected. As the potential is made more negative we observe that the intensity of a band at $145$ cm$^{-1}$ increases. At these potentials, the surface is being increasingly covered with underpotentially deposited lithium. Due to the sign convention used in these spectra the increase in intensity is an indication of the loss of absorption by a species, here the gold adatom on the gold surface. The close correspondence between the observed $145$ cm$^{-1}$ frequency and that calculated for a gold atom vibrating against an infinite mass suggests that the adatom is bonded to a single surface atom, that most of the motion involved in the optically active vibration occurs on the adatoms, and that the force constant is nearly the same on the surface as the gas-phase dimer.

At $440$ cm$^{-1}$ (Fig. 2), a simultaneous and parallel increase in absorbance occurs. This compares to a vibrational frequency of matrix-isolated $^{197}$Au$^7$Li of $705$ cm$^{-1}$.

Fig. 1. Surface far infrared difference spectrum of the system described on $130$–$170$ cm$^{-1}$ region as a function of electrode potential. The curves represent potentials of (top to bottom) $-1.70$ V, $-1.90$ V, $-2.60$ V, and $-2.90$ V respectively. Reference potential $-1.50$ V.
Fig. 2. Surface far infrared difference spectrum of the system described in Fig. 1 in the 200–700 cm\(^{-1}\) region as a function of electrode potential. The curves represent potentials of (top to bottom) –1.70 V, –2.90 V, and –3.0 V respectively. Reference potential –1.50 V.

and probably corresponds to a gold-lithium surface species. The diatomic gold–lithium molecule probably derives much of its high vibrational frequency and large bond strength (2.92 eV) [5] from ionic interactions, Li\(^{+}\)Au\(^{-}\). This is expected since apart from the halogen atoms, gold has the highest electron affinity of any element (2.31 eV) [6]. On a surface or in the bulk, the electron donated to gold may be delocalized into the gold conduction band, resulting in a smaller Coulombic force between the atoms in Li–Au (surface) than in diatomic Li–Au. Other explanations are possible, of course, but this does explain the lower than expected value for the Li–Au vibrational frequency, however.

No bands attributed to Li–Li vibrations are observed at potentials more positive than those required for bulk deposition of lithium. As soon as three dimensional growth of lithium begins, however, a band at 395 cm\(^{-1}\) rapidly grows in. This may be compared to the Li\(_2\) vibrational frequency of 351 cm\(^{-1}\) in the gas phase [3]. The shift of 44 cm\(^{-1}\) to higher frequency is relatively small considering that it corresponds to condensation of a dimer onto a solid surface. It is therefore probable that the 395 cm\(^{-1}\) peak does correspond to a surface vibration of Li–Li.

A cell was equipped with a very small electrode (0.5 mm diameter) so that the time constant of the cell could be decreased to suitably small values, and time resolved spectra were obtained for the fact nucleation and growth process of lithium on gold. Figure 3a shows the time and wavenumber resolved spectral response obtained at 10 ms intervals following application of the potential. The time profile alone is shown in Fig. 3b. The growth of the absorption transient follows a t\(^3\) dependence (a plot of absorbance/t\(^3\) vs. t is linear with a correlation coefficient = 0.9989). With this information, one may consider various models of nucleation and crystal growth to determine which possibilities are consistent with this time depend-
In this particular example, one finds that a mechanism involving instantaneous nucleation of lithium atoms followed by three-dimensional growth is consistent with the observed time dependence. One also notes that the absorption peak broadens as it grows, as a result of lateral interactions and surface defects which are incorporated into the new-grown crystallite.

In addition to the metal stretch bands reported in this note, we point out that there are other bands observed in other regions of the infrared spectrum. These correspond to adsorbed supporting electrolyte and solvent, as is evidenced by changing the system components. The behavior and nature of these vibrations will be the subject of a forthcoming report.

In conclusion, we have shown that two new powerful variations of infrared spectroelectrochemistry may be used for the study of fast reactions at metal surfaces involving direct bonding to the metal surface. Finally, we report the direct observation of metal atom vibrations at surfaces by reflection FTIR spectroscopy.

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REFERENCES

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