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Method for obtaining the Raman spectrum of a thin film on a metal surface*

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Abstract—A system for securing the laser-Raman spectrum of a thin layer on a reflecting metal surface is discussed. The general design considerations are specifically illustrated for a thin layer on silver using a 4880 Å laser exciting line. For this case the optimum angle of incidence for laser illumination is calculated to be 70° and the optimum angle for collection of the Raman-scattered light is around 60° from the surface normal. The sensitivity of the method is illustrated by showing two lines from the Raman spectrum of a 50 Å-layer of benzoic acid on a silver film.

1. INTRODUCTION

REFLECTION-absorption spectroscopy shows promise of being able to investigate adsorbed layers on metal surfaces, producing spectra analogous to the usual i.r. absorption spectra [1–3]. It would be extremely useful to be able to obtain the Raman spectra of such thin layers. This paper investigates the possibility of obtaining a reflection-Raman spectrum of a thin film on a metal surface.

The advantages of the Raman approach, either separately or in conjunction with infrared spectroscopy are well known. Some work has been done obtaining the Raman spectra of various molecules adsorbed on oxide surfaces [5–10] which are transparent to the laser light; however, the Raman study of adsorption on metal surfaces involves some peculiar problems which we shall discuss. The purposes of this paper are: (a) to consider those problems theoretically, in order to identify significant factors for the design of an appropriate experimental system; (b) to describe the design of an experimental system; (c) to describe some results from experimentally deposited films which give an indication of the sensitivity of this method for obtaining the spectra of thin films.

2. THEORETICAL CONSIDERATION OF A SINGLE REFLECTION

For historical reasons we have approached the problem by analogy with the reflection-absorption problem. An earlier paper [11] develops the argument that

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a beam of light reflected from a metal surface at normal incidence produces an electric standing wave field which has a node approximately at the surface of the metal. Molecules located on the surface (at the node in the standing wave electric field) cannot interact with the field and, hence, cannot absorb energy. For an appropriate, high, angle of incidence, the incident and reflected electric field vectors combine to give a resultant standing wave field with a significant amplitude

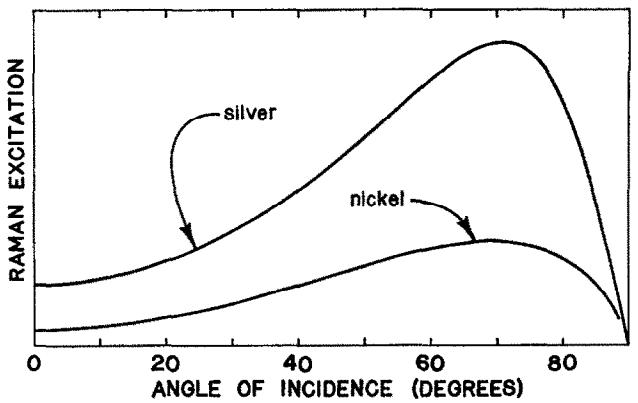

Fig. 1. The Raman excitation intensity of thin films on silver and nickel resulting from the standing wave field of 4880 Å laser light. The results are calculated for the laser light, polarized parallel to the plane of incidence, as a function of the angle of incidence.

at the surface, largely normal to the surface. In that paper, the emphasis was on i.r. absorption but a similar standing wave field is produced by the laser beam which is used to produce Raman scattering from molecules at the surface. In the earlier problem, the evidence for a large standing wave field at the surface is the high absorption of infrared radiation; in the laser case, it should be high intensity Raman scattering. We have used the same calculation as for the i.r. problem [11] and assume that the Raman excitation is proportional to the standing wave intensity which is also proportional to the calculated i.r. absorption. In the calculations we use optical constants which are appropriate for the wavelength of the laser light [12]. Figure 1 shows this dependence of the Raman excitation on angle of incidence for both silver and nickel substrates, calculated for the blue 4880 Å line of an argon–krypton ion laser. (We show experimental results only for silver substrates but show calculations for nickel as an indication of how critically the results depend on the metal being used.) Only the results for light polarized with the electric vector parallel to the plane of incidence are shown. Ref. [11] shows that the perpendicular polarization is not useful in this arrangement. The graph of Fig. 1 shows a maximum at about 70 degrees for silver and shows low excitation for normal or grazing illumination.

The second half of the theory of the Raman reflection problem is to consider the

[12] This reflectivity is calculated for the parallel polarization using optical constants from the *American Institute of Physics Handbook*, 2nd ed., sec. 6, p. 117 (1963).

intensity of the Raman-shifted light, at some distance from the surface. In this case the reflecting surface may produce some significant effects. The resultant standing wave field produced by the laser beam is largely perpendicular to the surface. In this treatment we will assume that the induced dipole of the surface molecules are, like the field, perpendicular to the surface. (Such induced dipoles may occur whether or not the permanent dipole of the molecule is perpendicular to the surface.)

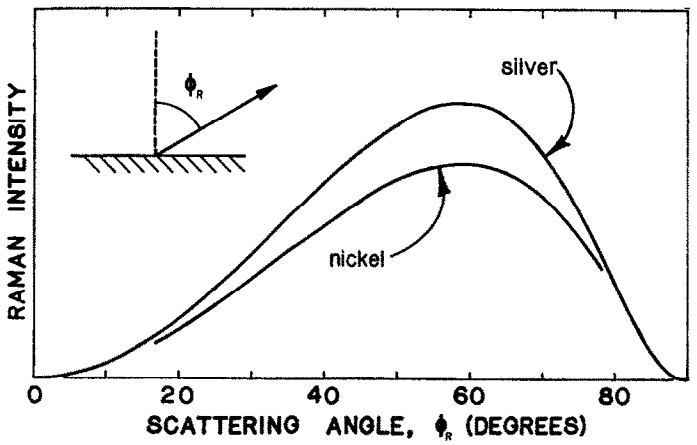

Fig. 2. The calculated angular intensity distribution of Raman-scattered light from thin films on silver and nickel for a wavelength of 4880 Å.

For purposes of calculation we would like to replace the Raman scattering mechanism with a dipole oscillating normal to the surface. To justify this picture, let us discuss a classical picture of the Raman scattering. The oscillating dipole moment of a surface molecule, induced by the laser radiation, has its amplitude modulated by some (lower frequency) natural vibration of the molecule. (The modulation mechanism is that the polarizability of the molecule varies with the vibrational motion.) Such an oscillating dipole should radiate energy. The resultant radiation pattern would be that of a dipole, oscillating normal to the surface, with its amplitude modulated by a natural vibration frequency of the molecule. The frequency analysis of such dipole radiation contains the laser frequency plus side bands, which are the Stokes and anti-Stokes lines of Raman scattering.

The appendix carries through the derivation of the variation of intensity of the Raman scattered light with angle. The results for silver and nickel are shown in Fig. 2. The graph shows the interesting result that the Raman intensity normal to the surface ($\phi_R = 0$) should be approximately zero, as it is also in the direction tangent to the surface ($\phi_R = 90°$). The peak comes around 60°.

The specification resulting from these two calculations is that when using the 4880 Å laser line to investigate a thin layer on silver, the angle of incidence of the laser beam ϕ_L, should be around 70° while the Raman scattered light should be collected at an angle, ϕ_R, around 60° to the surface normal. Using this information, we need to design a system which uses many reflections of the laser beam and which has a geometry allowing the Raman-scattered light to be collected at the appropriate angle and focussed on the entrance slit of a spectrometer.

3. SAMPLE SYSTEM DESIGN

Obviously there are many possible system designs. We will illustrate some of the more important considerations for a system design by discussing the particular problem of a silver substrate to be used with a Spex Ramalog 1401 spectrometer.

The sample system illustrated in Fig. 3 has some attractive features. By

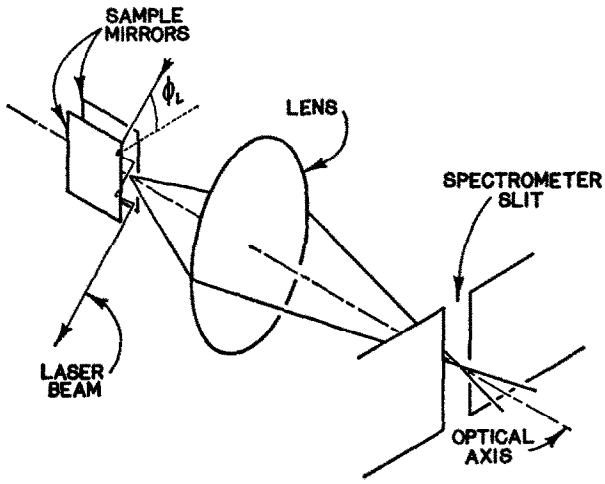

Fig. 3. Schematic view of a possible reflection-Raman system.

placing the sample mirrors close together, we can get many reflections, all at $\phi = \phi_L$. The opening between the mirrors serves as a source aperture of an appropriate shape to be imaged on the entrance slit of the spectrometer. The Raman-scattered light from each reflection of the laser beam is within a few reflections of getting out from between the sample mirrors.

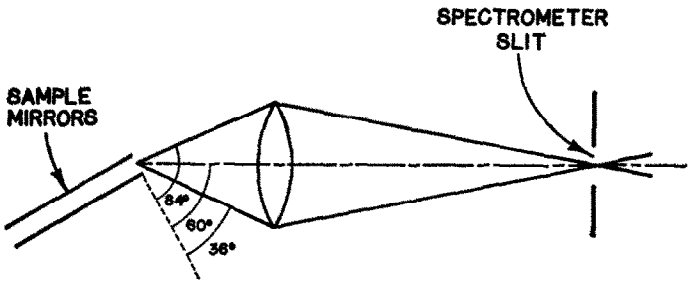

Fig. 4. Top of an improved reflection-Raman system.

The Spex 1401 instrument accepts an $f/5.6$ beam of light. With a source-to-slit magnification of 6, we therefore collect, from the sample mirrors, a beam of light with a half angle of 24°. Using the arrangement illustrated in Fig. 3, this beam would include the Raman-scattered light with angles, ϕ_R, ranging from about 66° to 90°. If we rotate the sample mirrors by 30°, as illustrated in Fig. 4, the range of angles, ϕ_R, collected by the lens goes from about 36°–84°. An examination of

Fig. 2 shows this to be a substantial improvement over the system of Fig. 3. A deficiency of the arrangement shown in Fig. 4 is that half of the radiation leaving the mirrors with ϕ_R between 36° and 84° escapes from the collecting lens. Figure 5 shows that this radiation may also be collected if the upper sample mirror is extended beyond the end of the other mirror. In this case the effective source aperture which must be imaged on the spectrometer slit has a width of $2d \cos \alpha$ where d is the distance between the source mirrors. For an α of 30° (as in Fig. 5) this implies an effective source aperture width of $1.7d$. If all the light emerging from between

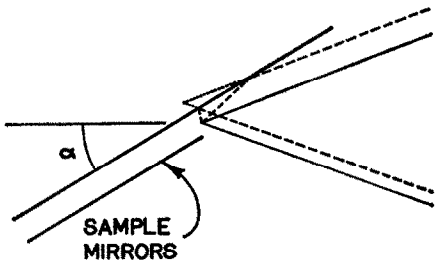

Fig. 5. Top view of a more efficient sample geometry for the reflection-Raman system.

the sample mirror is to get into the spectrometer, the magnified image of this effective source aperture should fall within the spectrometer slit opening. For a source-to-slit magnification of 6, this requires a slit width of $6 \times 1.7d = 10.2d$. The maximum slit height of the spectrometer is 50 mm. For the magnification of 6, this implies a sample mirror height of $50/6 = 8.3$ mm.

What is the optimum spacing of the sample mirrors? If we assume that the spectrometer slit width is always adjusted to match the magnified image of the effective source aperture, wider mirror spacing results in poorer spectrometer resolution. Narrower spacing permits better spectrometer resolution and more reflections of the laser beam as it passes between the sample mirrors. The reflectivity of silver is calculated [12] to be 0.961 for $\phi_L = 70°$ at 4880 Å. An appropriate spacing might be considered to be one which would provide enough reflections to effectively 'use up' the laser beam energy in one traverse of the sample mirrors. For $\phi_L = 70°$ a spacing of 0.10 mm would result in an attenuation of the beam intensity to about 30% of its original value in one traverse of the sample plates; while a spacing of 0.05 mm would reduce the intensity to about 10%. The beam of the laser we are using (Coherent Radiation model 52, argon–krypton ion laser) is about 3 mm in diameter and so must be focussed with a lens to get it between the closely-spaced mirrors. We have used a cylindrical lens to focus the beam to a line 3 mm long, rather than focussing it to a point. This should spread the beam over a wider area of the thin film to reduce the thermal effects of the laser beam.

Figure 6 attempts to show, schematically, the entire sample system which we used. The rotatable mirror provides the fine adjustment necessary to locate the focussed laser beam in the space between the two mirrors. All the auxiliary sample apparatus, including the fixed and adjustable mirrors are mounted on a point-slot-plane base which can be lifted out of the spectrometer source housing, freeing the instrument for conventional use.

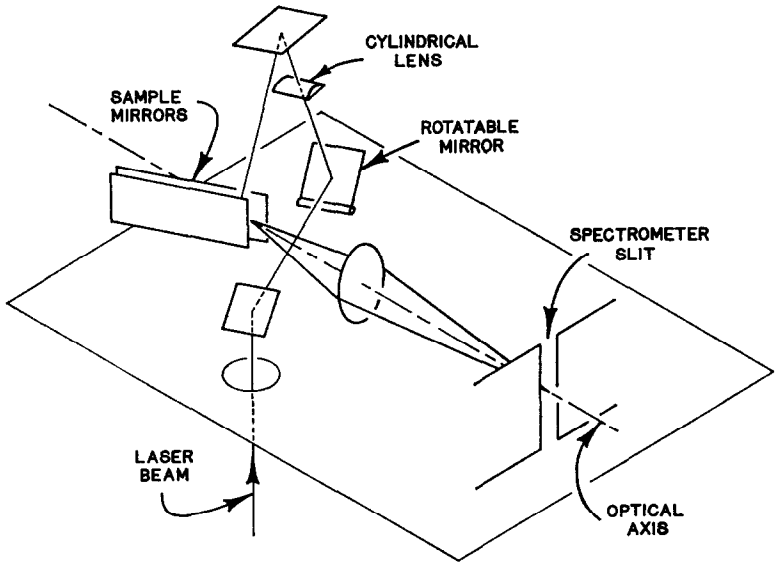

Fig. 6. Schematic diagram of the reflection-Raman sample system used in this work.

4. Experimental Procedures and Results

The focussing of the sample mirror onto the spectrometer slits is greatly facilitated by viewing the slits and source image from behind the entrance slits, using a periscope attachment sold by Spex Industries, Inc. The effective source aperture is bounded by the edge of the shorter sample mirror and its image as seen by reflection in the larger mirror. Using the periscope, this aperture can be imaged accurately and unambiguously on the spectrometer slit. Different sample mirror spacings are achieved by putting metal shims between the mirrors and holding them together with springs.

The theoretical treatment has given some insight into optimum parameters for the sample geometry but no information about the expected Raman intensities. To check the feasibility of this approach to the study of thin films, we prepared silver sample mirrors (by thermal evaporation of silver onto glass) and then applied a layer of benzoic acid. The benzoic acid in water solution was sprayed on the plates with an artist's air brush. The film thicknesses were calculated from the amount of material which was sprayed over a known area (an area much larger than the sample plates). The results shown here were obtained with sample mirrors 10 mm high and a ϕ_L of about 75° rather than the 8.3 mm and 70° prescribed by the foregoing analysis. These small differences, which resulted from lack of foresight rather than intention, should not make an important difference in the results.

Figure 7 shows the variation of the peak intensity of the 1010 and 1610 cm^{-1} Raman lines of benzoic acid with sample mirror spacing. Note that some of the fall-off of peak intensity at greater spacings results from the broadening of the recorded band due to the wide spectrometer slits. (The spectrometer slits in each case match the magnified source aperture.)

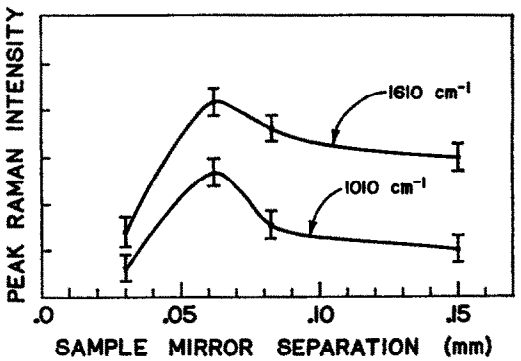

Fig. 7. Peak intensity for two Raman lines of a benzoic acid layer on silver, measured as a function of sample mirror spacing.

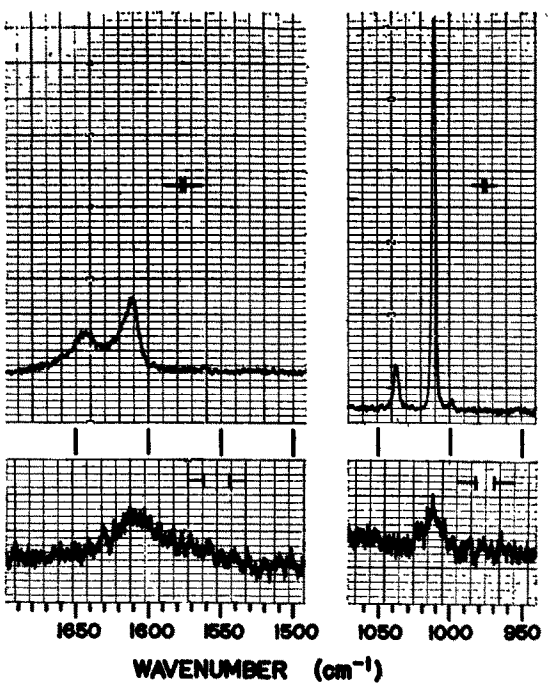

Fig. 8. Top: Two Raman lines of benzoic acid crystals in a capillary sample tube. Bottom: The same Raman lines for a 50 Å-thick layer of benzoic acid on silver. The spectral slit widths are indicated on each spectrum. The power of the 4880 Å laser exciting line is measured to be 6 mW at the sample mirrors.

From the data of Fig. 7 we chose a spacing of about 0.06 mm as a compromise between Raman intensity and spectrometer resolution. This spacing agrees well with the prediction of an appropriate spacing based on the reflectivity of silver; i.e. at this spacing, the beam energy is essentially used up in one traverse of the sample mirrors.

Figure 8 shows the 1010 cm^{-1} and 1610 cm^{-1} bands of benzoic acid for a 50 Å-thick film as calculated from the weight of the deposit. In the same figure a Raman spectrum of the bulk material is shown for comparison.

5. Discussion

The Raman bands of benzoic acid are clearly visible in Fig. 8 with a signal-to-noise ratio of 2 or 3. They are considerably broadened by the relatively wide slits used in this experiment. The test of sensitivity is somewhat biased in favor of the technique, in that benzoic acid is a fairly strong Raman scatterer and silver has a high reflectivity, making it a desirable substrate.

One aspect of the experimental test that is open to criticism is the description of the benzoic acid deposit by giving its effective film thickness. The amount of material deposited is estimated to be correct to within $\pm 30\,\%$, but it probably is not spread over the surface as a uniform thin film. We would expect it to exist as a series of small crystallites rather than a continuous film. Under the conditions we have established to optimize the intensity for a thin film, we should suffer a loss in Raman-scattered intensity if the material is distributed as thicker, separate particles.

The measured intensity of the exciting line incident on the sample mirrors was 6 mW, when the results shown here were obtained. With appropriate adjustment, this intensity can be increased by a factor of 3 or 4 giving an increase in signal-to noise ratio; or, alternatively, an increase in the sensitivity in detecting a thin film.

The conclusion we would draw from this experimental check is that the technique appears to be sensitive enough for some applications where the layers of interest are tens of angstroms thick. Whether it is actually sensitive enough to be used on a monolayer adsorbed on a metal surface still remains to be seen.

Appendix

We are assuming that the angular intensity distribution of Raman scattering for a molecule near the metal surface is like the radiation distribution of a dipole, oscillating normal to the surface. The model, illustrated in Fig. 9, shows the dipole located 'near' the surface; by which we mean that the distance between the surface and the dipole is small compared to the wavelength of the emitted radiation. The amplitude of the wave radiated in the direction ϕ is obtained by adding the direct wave and the reflected wave with appropriate amplitudes and phase factors. Since the dipole is located 'near' the metal surface, the phases of the two waves differ only by the reflection phase shift. On this model the amplitudes of the waves are determined by the radiation pattern of a radiating dipole (amplitude proportional to $\sin \beta$—see Fig. 9) and by the reflectivity of the metal surface. The resultant intensity of the radiation will be obtained by squaring the amplitude of the wave which results from the combination of the direct and reflected waves. For convenience we will let the amplitude of the wave radiated at right angles to the dipole direction be unity. Hence, all intensities will be calculated relative to the maximum intensity of the isolated radiating dipole.

Let A_1 and A_2 be the amplitude of the direct and reflected ray. Let A be the resultant amplitude.

δ and r are the reflection phase shift and the amplitude reflectivity for radiation polarized parallel to the plane of incidence.

From Fig. 9

$$I = A^2 = A_1^2 + A_2^2 + 2A_1A_2 \cos \delta$$

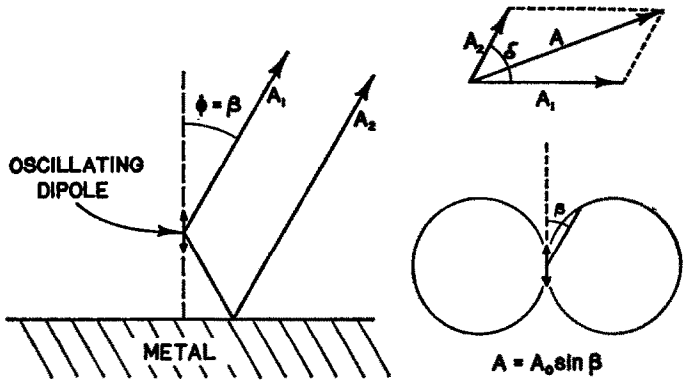

Fig. 9. Left: Model for Raman-scattered intensity (an oscillating dipole located near a metal surface). Lower Right: Amplitude of radiation from an oscillating dipole as a function of angle. Upper Right: Addition of amplitude for direct and reflected beams.

where

$$A_1 = \sin \phi,$$
$$A_2 = r \sin \phi.$$

The values of δ and r can be calculated [13] from the optical constants of the metal using the expressions,

$$\tan \delta = \frac{2b \cos \phi (a^2 + b^2 - \sin^2 \phi)}{a^2 + b^2 - (n^2 + k^2)^2 \cos^2 \phi}$$

and

$$r^2 = \frac{[(n^2 - k^2) \cos \phi - a]^2 + [2nk \cos \phi - b]^2}{[(n^2 - k^2) \cos \phi + a]^2 + [2nk \cos \phi + b]^2},$$

for a and b defined by

$$a^2 = \tfrac{1}{2}\{[(n^2 - k^2 - \sin^2 \phi)^2 + 4n^2k^2]^{1/2} + n^2 - k^2 - \sin^2 \phi\}$$
$$b^2 = \tfrac{1}{2}\{[(n^2 - k^2 - \sin^2 \phi)^2 + 4n^2k^2]^{1/2} - n^2 + k^2 + \sin^2 \phi\}.$$

In these equations the complex index of refraction is defined as $\tilde{n} = n - ik$.
The intensity, I, calculated by this method is what is plotted as Raman intensity in Fig. 2.

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