A New Surface for Surface-Enhanced Infrared Spectroscopy: Tin Island Films

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For the first time, it has been observed that tin island films used in surface infrared experiments give rise to an electromagnetic enhancement of the infrared absorption spectrum. The surface enhancement of the infrared (SEIR) absorption by tin island films is shown for evaporated nanometric films of 5,14-pentacenedione (Q2) and naphthalic 1,8:4,5-dianhydride (NTCDA). The experiments and spectral characteristics demonstrating the ability of tin to produce SEIR of organic molecules physically adsorbed onto tin structures are described. Tin island films of varying mass thickness were fabricated to ascertain maximum enhancement. Their morphology was determined by transmission electron microscopy. Comparisons are made between the SEIR spectra on rough tin and on silver surfaces and the corresponding reflection−absorption spectra (RAIRS) obtained for the same organic molecules on reflecting surfaces of tin and silver.

Introduction

Surface-enhanced vibrational spectroscopy (SEVS) is the study of molecular vibrations of molecules adsorbed on surfaces that can enhance the absorption and the emission of electromagnetic radiation. Twenty years after its discovery, surface-enhanced Raman scattering (SERS) is a well-developed analytical technique. Its development and the initial efforts are compiled in two basic reference books.[1,2] An early report by Hartstein et al.[3] showed that silver films could also be used to do surface-enhanced infrared (SEIR). However, SEIR did not reach the same level of development of SERS. In fact, the bulk of the SEIR activity is quite recent and the field is just starting to blossom. It is easy to see that due to the vast body of infrared vibrational data that has been systematically collected for gas, liquid, and solids, any improvement in the sensitivity of surface-infrared spectroscopy is bound to have a major impact in the field of vibrational spectroscopy of molecules on surfaces.

Enhancement Factor. The enhancement of vibrational intensities (Raman or infrared) is commonly discussed in terms of two separate contributions: the electromagnetic enhancement mechanism that has been clearly formulated allowing electrodynamic calculations of the surface-enhanced electric intensities,[4−6] and the perturbations in the optical parameters of the adsorbate (chemical effect).[7] Therefore, observed intensities in SEVS are proportional to the product of these two main contributions that may be written as follows:

$$\text{SERS} \propto |A(\omega_L)|^2 |A(\omega_E)|^2 |\partial\alpha/\partial Q|^2$$

$$\text{SEIR} \propto |A(\omega)|^2 |\partial\mu/\partial Q|^2$$

In SERS the $A(\omega_L)$ and $A(\omega_E)$ are the enhanced-absorption and the enhanced-emission factors at the frequencies ω_L and ω_E, respectively. $|\partial\mu/\partial Q|$ is the magnitude of the dipole moment derivative with respect to the Q normal coordinate. Since SEIR can only benefit from the $|A(\omega)|^2$ factor, the total SEIR enhancement is expected to be orders of magnitude smaller than the enhancement factor observed in SERS. For instance, in the original report of Hartstein et al.,[3] the maximum enhancement factor (EF) measured for SEIR was 20 using ATR and silver islands. Osawa and Ikeda[8] also report an electromagnetic EF of 20−30 for transmission IR spectra on silver islands and an enhancement factor of 20−50 for the case of reflection−absorption SEIR.[9] In our own SEIR work on silver island films the optimum EF was found to be ca. 30.[10] In the present work the best EF factor measured for Sn island films was 20.
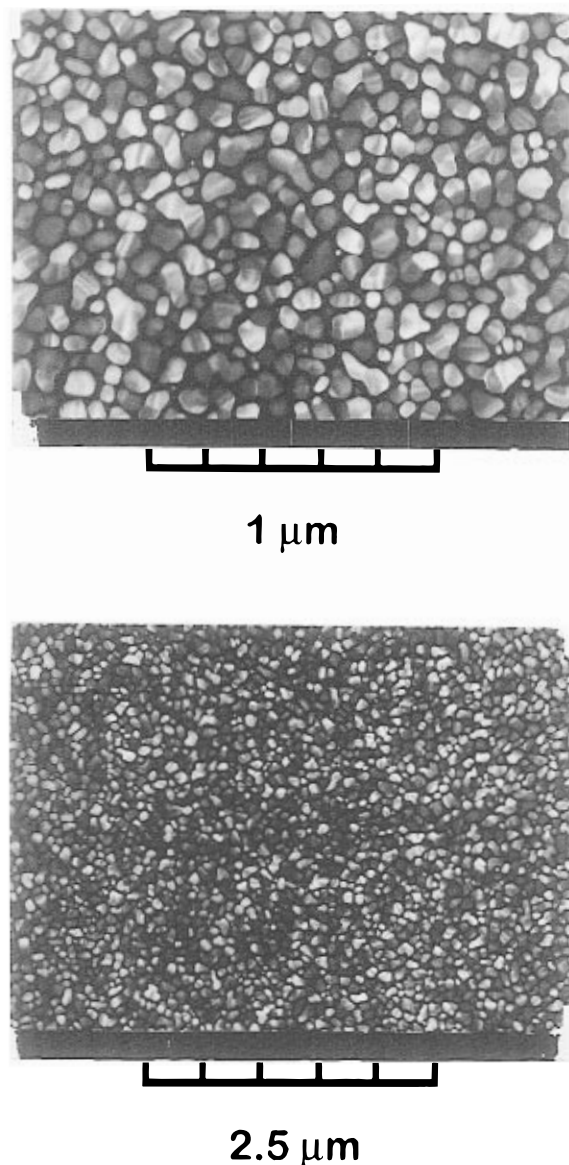
Substrate. According to the electromagnetic mechanism used for the evaluation of the enhancement factor on rough surfaces, the activity of the *substrate* strongly depends on the *shape* of surface protrusions (or metal particles) and the *dielectric function* of the material in the spectral region of interest. In the visible region, silver is the most commonly used SERS substrate,[11] and silver surfaces continue to be actively investigated by many groups.[12] Single particle models and the effective medium theories can also explain the enhancement observed on silver island films in the infrared region.[9,13] It is important to point out that the electromagnetic interpretation also predicts surface enhancement for rough semiconductor surfaces,[14] which would allow enhancers for specific regions of the electromagnetic spectrum to be screened. In particular, rough surfaces of tin were never considered as SERS active surfaces in the visible or near-infrared regions of the spectra. In our group Sn was used in SERS experiments to provide the underlying shape in the fabrication of silver-coated tin spheres.[6] In this technique, opaque tin films of 150 nm mass thickness are fabricated to form very regular tin spheres that can be easily coated with silver. Therefore, the tin provides the shape while the silver coating gives the plasmon absorption in resonance with the visible laser excitation, a necessary condition for the local field enhancement.

Tin has a density of 7.2984 g/cm³ and the difference between its melting point 231.9 °C and its boiling point 2270 °C is one of the widest of any metal. The common β phase (white tin) can be easily evaporated to form island films with regular shape. It is also known that for tin an absorption series exists in the near-infrared and in the infrared spectral region. The objective of the present work is to show that tin structures of ultrathin films (18 nm mass thickness) can enhance the absorption of infrared radiation adding a new active substrate for SEIR.

Experimental Section

The samples for transmission FTIR experiments were prepared by vacuum evaporation of 15 and 18 nm mass thickness

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Figure 1. Transmission electron micrographs of a 18 nm tin island film.

Figure 2. Transmission FTIR spectra of 15 nm mass thickness films of pentacenedione evaporated onto a 18 nm tin island film and onto the KBr substrate.
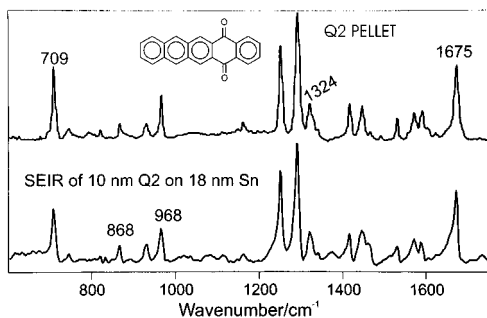
cm^{-1} resolution with a sample box pressure of 5 Torr. The reflection spectra were obtained by using a Spectra-Tech variable angle reflectance accessory and an incidence angle of 75°.

Results and Discussion

Surface-Enhanced Infrared of 5,14-Pentacenedione. The electromagnetic enhancement mechanism (EM) allows one to calculate, to different degrees of approximation, the enhancement that a particular surface could provide for SEVS. It can be shown that certain metals may be used to enhance optical properties of adsorbed molecules in the visible, in the near-infrared, and/or in the infrared region of the spectrum. Tin, with a low melting point and a high surface tension, can provide island films with very regular particle shape that can be easily fabricated by vacuum evaporation. It is known that tin absorbs light in the near-infrared and infrared regions of the spectrum. These two factors are necessary conditions for enhancement according to the electromagnetic mechanism. Tin island films of varying thicknesses were fabricated and coated with 10 or 15 nm mass thickness of the organic Q2 or NTCDA. The enhancement of the infrared absorption spectra was observed for tin films of various thicknesses; however, the best results were obtained with tin island films of 15 and 18 nm mass thickness. The SEIR of a 15 nm film of Q2 on 18 nm tin film is shown in Figure 2. The spectrum of Q2 film deposited under identical conditions on the substrate without tin is also shown in Figure 2 for comparison. The maximum enhancement factor observed was ca. 20.

In order to facilitate the discussion of the spectroscopic data, a brief discussion of the vibrational assignment of the observed fundamental vibrational wavenumbers is necessary. The Q2 molecule belongs to the C_{2v} point group of symmetry with a total irreducible representation $\Gamma = 35a_1 + 17a_2 + 16b_1 + 34b_2$. The infrared-active vibrations a_1 are polarized along the z (long) molecular axis, the b_2 fundamentals are polarized along the y (short) molecular axis and the b_1 species are the out-of-plane normal modes. The a_2 are not infrared active. Following the report of Brivina et al.[15] for the assignment of normal modes of 6,13-pentacenedione, and with the help of the semiempirical methods AM1 and PM3 implemented in HyperChem and Gaussian for computations of the vibrational spectrum, the assignments of the most intense IR wavenumbers are given in Table 1. The assignment of in-plane and out-of-plane vibrations is important to describe the properties of the SEIR spectra in comparison with the corresponding reflection–absorption spectra and transmission FTIR spectra of solid matrices and thin solid films.

As pointed out in the Introduction, the enhancement of the vibrational intensities in the mid-infrared may be the result of two contributions. The enhanced absorption cross section is

of tin onto KBr disks and ZnS and Ge substrates. The tin was evaporated under a base pressure of 4×10^{-6} mbar while the temperature of substrates was held at 80 °C. The bulk density of tin employed was 7.3 g/cm^3, the tooling factor 105%, and the Z ratio 0.724. The tin evaporation rate was maintained at 0.5 nm/s, and film thickness was monitored using an XTC Inficon quartz crystal oscillator. Transmission electron microscopy of the tin island films was obtained in a JEOL 100CX TEM with 100 kV. The TEMs of an 18 nm tin film recorded at 50K and 20K magnification are shown in Figure 1.

The smooth reflecting metal substrates used for RAIRS measurements were prepared by vacuum evaporation of 150 nm mass thickness of tin and 100 nm of Ag onto Corning 7059 glass slides. The reflecting surfaces were coated by vacuum evaporation with 40 nm thick films of 5,14-pentacenedione (Q2) and naphthalic 1,8:4,5-dianhydride (NTCDA). The film thickness and deposition rate were monitored using the aforementioned system. The organic films, deposited by vacuum evaporation onto the metal island films of Tin and Ag, varied between 10 and 15 nm mass thickness.

All the infrared spectra were recorded using a Bomem DA3 FTIR equipped with a liquid nitrogen cooled MCT detector. Spectra were recorded using the co-addition of 1024 scans at 4

Figure 3. SEIR difference spectrum and the transmission spectrum of Q2 in a CsI pellet.

TABLE 1: Internal Coordinate Assignments for Selected Infrared Wavenumbers of 5,14-Pentacenedione (Relative Intensities in Parentheses)

| KBr pellet	SEIR	RAIRS	assignment
709 (38)	710 (41)	707 (6)	out-of-plane wag b_1
743 (5)	748 (2)	748 (1)	out-of-plane wag b_1
866 (5)	868 (11)	866 (1)	out-of-plane wag b_1
967 (19)	968 (15)	968 (32)	C—H bending a_1
1254 (56)	1254 (52)	1257 (46)	ring str + C—H bend a_1
1294 (100)	1294 (100)	1299 (100)	ring str + C—H bend b_2
1324 (19)	1323 (19)	1321 (24)	ring str + C—H bend b_2
1421 (18)	1421 (21)	1421 (31)	ring str b_2
1452 (16)	1453 (18)	1452 (28)	ring str a_1
1534 (9)	1533 (10)	1535 (15)	ring str b_2
1574 (10)	1576 (5)	1577 (3)	ring str a_1
1592 (9)	1593 (4)	1591 (3)	ring str b_2
1675 (56)	1676 (18)	1672 (5)	C=O str b_2

produced by changes in the metal response to electromagnetic radiation, and changes induced in the dipole moment derivatives of each fundamental vibrational mode. The chemical effect or change in the dipole moment derivatives due to the adsorbate— surface interaction may be neglected for physically adsorbed molecules; but it should be carefully examined for chemically adsorbed molecules. Experimentally, chemical adsorption results in frequency shift and/or band broadening, most particularly of the functional group directly involved in the adsorbate-surface interaction. Figure 3 illustrates the comparison between the SEIR spectrum and the spectrum of the Q2 dispersed in a CsI pellet. The observed wavenumbers for the a group of intense infrared active vibrations for both spectra are given in Table 1. There is no evidence of chemical interaction and the same wavenumbers are measured in the two experimental spectra. It may be concluded that Q2 is physisorbed onto the tin surface and, correspondingly, there is no chemical contribution to the observed enhancement. The EF found for Q2 on tin is therefore due to the electromagnetic mechanism. The relative intensities of the SEIR spectrum shown in Figure 3 are the result of the subtraction of the spectrum of the nanometric film on the IR transparent substrate from the SEIR spectrum of the same film on tin. The analysis of the FTIR transmission spectra given in Figure 3 indicates that the SEIR spectrum does not contain any additional bands or any considerable band shift with respect to those bands present in the IR spectrum of the CsI pellet.

　The transmission infrared spectra of nanometric evaporated films of Q2 onto KBr and ZnS substrates show a different pattern of relative intensities when compared with the SEIR as seen in Figure 2. The distinct pattern of the spectrum of the film may be due to molecular organization, producing as a result a polarized IR spectrum.
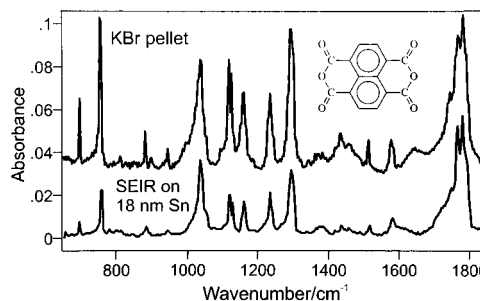
　Finally, for a complete characterization of the SEIR on tin two additional experiments were carried out. First, it was important to obtain the RAIRS spectrum on a smooth tin surface.
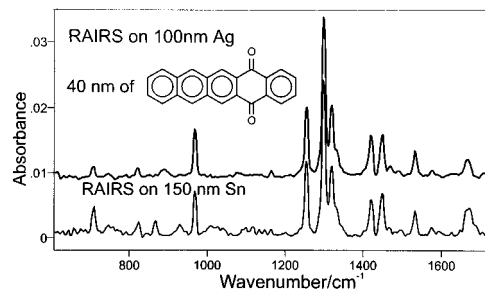
Figure 4. RAIRS spectra of 40 nm of Q2 on 150 nm of tin and on 100 nm Ag.
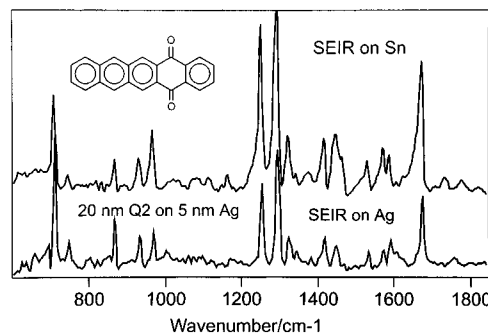
Figure 5. SEIR of Q2 on tin and Ag island films.

Figure 6. SEIR of NTCDA on 18 nm tin island film and transmission FT-IR of NTCDA pellet in KBr.

A tin mirror was fabricated by depositing 150 nm of tin onto a glass substrate and then coated with 40 nm of Q2. The RAIRS spectrum is shown in Figure 4. The RAIRS of 40 nm Q2 film on a silver mirror is also shown in Figure 4. In RAIRS only those vibrational modes with a component of the dipole moment derivative perpendicular to the surface can be observed. Since the out-of-plane vibrational modes observed below 968 cm^{-1} are present in RAIRS with lower relative intensity, the molecular organization is predominantly with an edge-on or head-on orientation. Identical RAIRS of Q2 on tin and Ag seems to indicate that the same molecular organization exist in the 40 nm organic film formed on smooth tin and Ag. A direct comparison of the SEIR spectrum of Figure 2, or the SEIR difference spectrum shown in Figure 3, with the RAIRS spectra (Figure 4), indicates that the RAIRS surface selection rules can not be directly extended to explain surface-enhanced infrared intensities. Second, the SEIR of Q2 on silver island film was also obtained and is presented in Figure 5 to be compared with the SEIR on tin. The results are encouraging since the SEIR obtained on two very different substrates are quite similar for the same physisorbed molecule.

　Surface-Enhanced Infrared of Naphthalic 1,8:4,5-Dianhydride (NTCDA). The new tin surface was also tested using molecules for which the SEIR spectra on Ag and Au island films have been obtained in our laboratory: NTCDA and perylenetetracarboxylic dianhydride, PTCDA.[16] SEIR was achieved for both molecules. The transmission SEIR spectrum

of NTCDA on tin islands (18 nm thickness) fabricated onto a ZnS substrate is shown in Figure 6. The spectrum of NTCDA KBr pellet is also included in Figure 6 for direct comparison. The latter spectrum is the absorption due to infrared resonances with a random spatial distribution of molecules and aggregates that should closely follow the prediction of the point group symmetry. Notably, the observed relative intensities in the SEIR spectra of these molecules on tin, Ag, and Au are closer to that of the solid matrices. They are, however, different from those observed in RAIRS or in thin solid films of the neat material on smooth infrared transparent substrates.

Conclusions

The use of tin island films for surface-enhanced infrared is illustrated in the tranmission geometry. Since the target molecule is physically adsorbed onto the tin surface, the enhancement factor of 20 is considered to be entirely due to electromagnetic enhancement. The SEIR on tin showed a different pattern of relative intensities when compared with the RAIRS spectra on smooth tin and Ag. It is possible that a number of other SEIR active substrates may be fabricated. The work in this direction is presently underway in our laboratory.

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