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ABSTRACT

Pacific Northwest Laboratory is developing a large-area chemical sensor that combines chemically selective coatings and optical spectroscopy to detect target compounds. The chemically selective material is incorporated into the cladding of an optical fiber waveguide. The material is interrogated using optical spectroscopic techniques to determine the concentration of target compounds. The optical interrogation method includes two spectroscopies: visible-near infrared absorption spectroscopy and Raman spectroscopy. This work develops the physical and mathematical models of such a sensor and provides a set of tools with which to make design predictions for the large-area chemical sensors. The theoretical relationships derived herein allow the use of bulk absorption parameters and bulk Raman coefficients to predict sensor performance.

INTRODUCTION.

Pacific Northwest Laboratory (PNL) is developing a large-area, fiber-optic chemical sensor. Although there is a wide variety of chemical-sensor concepts which use optical fibers, this concept is believed to be the first to combine chemically selective coatings and optical spectroscopy. Although, the sensors under development are designed to detect compounds which are associated with nuclear proliferation activities (primarily iodine-bearing compounds and organophosphates), the technology has many other possible uses.

The chemically selective material is incorporated into the cladding of an optical fiber waveguide. The material is interrogated using optical spectroscopic techniques to determine the concentration of target compounds. This approach combines the effectiveness of selective coatings with the precision of spectroscopic analysis, thereby avoiding interference and calibration problems associated with many chemical sensors designed for field use.

The optical interrogation method includes two spectroscopies: visible/near-infrared absorption spectroscopy and Raman spectroscopy. In many ways, these are complementary techniques. Visible/near-infrared spectroscopy takes full advantage of the wavelength regime of maximum transparency for silica-based waveguides. If the selective coating has an associated color change when reacted, this can be detected via visible light absorption. Many organic molecules have highly characteristic spectra in the near infrared also. For species with absorption features in the mid-infrared region, other-than-silica fibers would be required; these are costly, difficult-to-handle, and subject to environmental degradation. Therefore, at present, absorption is not considered for the optical-interrogation method for those species.

Raman spectroscopy takes place over a wavelength regime centered on the laser probe used, and so the experimenter can collect data where the fibers are most transparent. Raman spectroscopy has the potential to yield detailed vibrational spectra of the target compounds; however, interfering Raman signals from the waveguide itself could make quantitative analysis difficult. Both absorption and Raman spectroscopy are well-understood for bulk materials.

This note outlines the development of the models necessary to extend the appropriate spectroscopic theory from bulk materials to waveguides. In the proposed sensor, the analyte will be selectively absorbed into the polymeric cladding of a silica waveguide. This geometry requires the light traveling down the core of the waveguide to interrogate the analyte indirectly via an evanescent field interaction. So, in addition to interacting with the analyte in a more complicated manner, the light traveling down the waveguide has many interactions with the core/cladding boundary. These two conditions make the waveguide spectroscopy proposed by this project very different from

conventional bulk spectroscopy.

SENSOR CONCEPTUAL MODEL

To produce a large-area chemical sensor, a material which selectively bonds to the target chemical species will be incorporated into a permeable cladding layer of a step-index fiber waveguide (Figure 1). In a step-index waveguide, the electromagnetic field of the light confined to the core penetrates into the cladding via an evanescent field. Mathematically describing the interaction of light in the core with molecules in the cladding will help determine various design criteria, such as the optimum length of the fiber sensor, the concentration of the selective coating required, and the ultimate sensitivity that can be expected.

Figure 1. Cross-section of a step-index waveguide-based chemical sensor that relies on evanescent field interrogation of the target compound.

Sensor interrogation. The target compounds will be detected and measured by using optical absorption and/or Raman spectroscopy by sending light down the core of the waveguide. Evanescent-wave absorption occurs when photons confined in the core of the waveguide are absorbed by molecules within the cladding. Evanescent-wave Raman scattering (EWRS) is a process in which photons confined in the waveguide core interact with molecules in the cladding. Energy is briefly deposited into the molecule and is quickly re-emitted back into the core, shifted in energy by a normal-mode vibration energy.

DEVELOPMENT OF THE PHYSICAL MODEL

This section will develop the mathematical relationship that can be used to make predications about the spectroscopy of molecules in the evanescent field of a multimode fiber waveguide. The product will be relationships which can predict the probability of absorption or Raman scattering

of a photon, per reflection, from the core/cladding interface, in terms of relevant bulk-medium parameters.

To do this, we will start with the Fresnel equations (which govern reflection of light at a boundary). From these, we will get the magnitude and dependence of the evanescent fields as a function of the reflection angle and other parameters. Then, using a semi-classical description of optical absorption, the evanescent-field absorption will be related to the empirical parameters of the Lambert/Beer law. The result will be an expression for the fraction of photons absorbed, per reflection, in terms of known or bulk properties of the molecule. Next using a second-quantized description of the Raman scattering process, we will develop a similar relationship for the fraction of the photons which are Raman shifted, per reflection, again in terms of bulk Raman coefficients.

In the step-index, multi-mode fibers which we use, the core is much larger than the wavelength of light, so a plane-wave representation will be used here. The development of the governing equations for the plane-wave basis will follow that of Jackson.¹ The units will be Gaussian units (cgs units). The Fresnel equations give us the relationship for the initial amplitude of the evanescent field (E_0') and reflected field (E_0''), at the core/cladding interface.

¹ The notation and units follow that of J. D. Jackson, *Classical Electrodynamics*, Wiley, 1962. (pg. 278 ff.)

E_0 Perpendicular to the Plane of Incidence. ($E_{\perp}$)

E_0 Parallel to the Plane of Incidence. ($E_{\parallel}$)

$$\frac{E_0''}{E_0} = \frac{Z \cos i - Z' \cos r}{Z \cos i + Z' \cos r}$$

and

$$\frac{E_0'}{E_0} = \frac{2 Z \cos i}{Z \cos i + Z' \cos r}$$

(1)

$$\frac{E_0''}{E_0} = \frac{Z' \cos i - Z \cos r}{Z' \cos i + Z \cos r}$$

and

$$\frac{E_0'}{E_0} = \frac{2 Z \cos i}{Z' \cos i + Z \cos r}$$

(2)

Here $Z = \sqrt{\frac{\epsilon}{\mu}}$ and $Z' = \sqrt{\frac{\epsilon'}{\mu'}}$. Here the unprimed variables are those for the medium in which the incident and reflected rays lie (the core); the primed variables are those in which the evanescent field acts (the cladding). Snell's law and the definition of the critical angle allow us to eliminate the refractive indices, viz. $\frac{\sin i}{\sin i_0} = \sin r$ where i is the angle of incidence, r is the angle of refraction, and i_0 is the critical angle. These results are correct even for angles greater than the critical angle. In that case, it follows that

$$\cos r = \sqrt{1 - \sin^2 r} = i \sqrt{\left(\frac{\sin i}{\sin i_0}\right)^2 - 1} \quad (3)$$

so that the propagation function becomes

$$\begin{aligned} \exp(i \mathbf{k}' \cdot \mathbf{r}) &= \exp(i \mathbf{k}' (x \sin r + z \cos r)) \\ &= \exp\left(i \mathbf{k}' x \frac{\sin i}{\sin i_0}\right) \cdot \exp\left(-k' z \sqrt{\left(\frac{\sin i}{\sin i_0}\right)^2 - 1}\right) \end{aligned} \quad (4)$$

Equation 4 gives us the variation of the amplitude of the evanescent field into the cladding.

Consider the evanescent-wave amplitude by substituting Equation 4 into the Fresnel equations for E_0' .

For $E_{\perp}$

$$\frac{E_0'}{E_0} = \frac{2 Z \cos i}{Z \cos i + i Z' |\cos r|} \quad (5a)$$

and for $E_{\parallel}$

$$\frac{E_0'}{E_0} = \frac{2 Z \cos i}{Z' \cos i + i Z |\cos r|} \quad (5b)$$

These are the amplitudes to be used for any modelling involving the evanescent field. For optical parameters appropriate to silicone-clad silica fibers ($n = 1.46$ and $n' = 1.41$), the (initial) evanescent-field amplitudes vary from approximately twice the core field (at the critical angle) to zero (for grazing incidence). For the modal ray, the evanescent field is approximately 1.5 times the core field. For the same fiber, the evanescent-field decay constant, as given by Eq. 4, for light at wavelength 632.8 nm, is about 4600 cm^{-1} for the modal ray; this varies from approximately 6000 cm^{-1} near grazing incidence to vanishing at the critical angle. Stated differently, the field penetration length (e^{-1} distance) varies from approximately 1.6 μm to infinity; for the modal ray, it is approximately 2.2 μm .

Absorption

To describe the absorption by a molecule at a distance, z , from the waveguiding surface, we want to relate the interaction of the evanescent field to the bulk optical absorption. To do this, we relate the absorption, as measured by bulk optical experiments, to microscopic variables relevant to our waveguide sensor.

A suitable description of absorption can be obtained by using a semiclassical model. In this approach, each spectral absorption peak is represented by a damped harmonic oscillator.² The parameters of the harmonic oscillator are the mass of the driven particle, m ;³ the resonant frequency, ω_0 ; the charge, q ; and the damping coefficient, γ . The equation of motion of the damped harmonic oscillator driven by an electric field, $E(z)$ is

$$m \frac{d^2x}{dt^2} = -m\omega_0^2 x - m\gamma \frac{dx}{dt} + q E(z,t) \quad (6)$$

The driving electric field is varying harmonically $E(z,t)$ in the equation of motion; using the fact that the harmonic oscillator will respond coherently with the driving force, we can solve for x and thence for $j(z)$ (the current density at z , assuming $N(z)$ per unit volume of the harmonic oscillators)

$$j(z) = \frac{-i \omega q^2 \left(\frac{E}{m} \right) N(z)}{(\omega_0^2 - \omega^2 - i \omega \gamma)} \quad (7)$$

Now the power, per unit volume, absorbed by the harmonic oscillators at z is

$$P(z) = \frac{1}{2} \operatorname{Re}(j \cdot E) = \frac{\frac{1}{2} e^2 \omega^2 \gamma E^2 N(z)}{[(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2]} \quad (8)$$

where we have set q^2 equal to e^2 . To relate Eq. 8 to macroscopic measured absorption coefficients, from the Lambert/Beer law $I = I_0 \exp(-\alpha Cx)$ (where α is the absorption coefficient and C is the concentration of the absorbing material) the power dissipated per unit volume is

$$P(z) = \alpha N(z) I(z) \quad (9)$$

Using Eq. 8, and

$$I = \frac{k \cdot S}{k} = \frac{ck}{8\pi k} \cdot (E \times H^*) = \frac{nc}{8\pi\mu} E^2 \quad (10)$$

(where S is the Poynting vector, n the refractive index and c is the speed of light) gives the relationship between α and the harmonic oscillator parameters.

$$\alpha = \frac{4\pi e^2 \omega^2 \gamma}{[(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2]} \quad (11)$$

² A full quantum-mechanical treatment gives essentially the same results.

³ For electronic transitions, the mass will be an effective electronic mass; for vibrational modes, the mass will be a reduced mass for the normal modes of the ions in motion.

Now we want to relate this to the loss on reflection. Locating the same harmonic oscillators in the region of the evanescent field, with density, $N(z)$, the energy loss, per unit time, is

$$\bar{P} = \frac{e^2 \omega^2 \gamma E_0^2(z) N(z)}{[(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma^2]} = \frac{E_0^2(z) N(z)}{4\pi} \alpha \quad (12)$$

So now we have the energy being dissipated from the reflected beam per unit time in terms of the Lambert/Beer law absorption coefficient. To get the absorption probability from this, we note that

$$I = (\text{the number of photons incident per unit area per unit time}) \times (\text{energy per photon}) \\ = (N_i) \times (\hbar \omega) \quad (13)$$

and

$$\bar{P} = (\text{the number of photons absorbed per unit time}) \times (\text{energy per photon}) \\ = (N_a) \times (\hbar \omega) \quad (14)$$

So the fraction of incident photons which are absorbed, per reflection, is

$$f = \frac{N_a}{N_i} = \frac{\bar{P}}{I} = \frac{2 N(z) \mu \alpha}{nc} \cdot \frac{E_0^2(z)}{E_0^2} \quad (15)$$

This relationship, together with Eqs. (5) will allow us to predict the evanescent absorption by a density $N(z)$ of target molecules at a distance z from the core/cladding interface. For an absorber uniformly distributed in the cladding of a 100- μm , silicone-clad silica fiber, the evanescent-field absorption per centimeter, for light with wavelength ca. 630 nm., is about 1% of that passing through a bulk sample of the same concentration.

Raman

This section will examine the Raman scattering in bulk media and under evanescent-field conditions in a waveguide. The discussion above also provides most of the theoretical basis for the Raman scattering as well.

Whereas the discussion of absorption is most easily performed using a classical model, that for Raman scattering is most easily done using quantum theory. An analysis of Raman scattering is most easily done in the second quantized formulation. In this basis, the vector potential, $A(x,t)$, is written

$$A(x,t) = \frac{1}{\sqrt{4\pi c^2}} \sum_i q_i(t) u_i(x) \quad (16)$$

where q_i is the generalized displacement and $u_i(x)$ is a field eigenfunction. The eigenfunction, $u_i(x)$, obeys the wave equation and boundary conditions for the problem, in this case, those appropriate to propagation in a cylindrical dielectric waveguide. The appropriate approximation is that these are represented by plane waves within the fiber waveguide and by the evanescent field appropriate to a plane wave outside the fiber. This is a good approximation for the case of evanescent-wave interactions in multimode fibers. For the time being, it suffices to note that these form a complete, orthonormal set.⁴ With these conditions, it is possible to show that the Hamiltonian for the radiation field becomes

⁴ W. H. Louisell, *Quantum Statistical Properties of Radiation*, Wiley, 1973.

$$H = \sum_n \hbar \omega_n (a_n^\dagger a_n + \frac{1}{2}) \quad (17)$$

The operators $a_1^\dagger$ and a_1 are, respectively, photon creation and annihilation operators. The electron-lattice Hamiltonian can be written in the same second-quantized format.

$$H = \sum_s \hbar \omega_s (A_s^\dagger A_s + \frac{1}{2}) \quad (18)$$

where the $A^\dagger$ and A are respectively, lattice-vibration creation and annihilation operators. Thus, the unperturbed Hamiltonian can be written⁵

$$H_0 = \sum_\alpha \epsilon_\alpha c_\alpha^\dagger c_\alpha + \sum_n \hbar \omega_n (a_n^\dagger a_n + \frac{1}{2}) + \sum_s \hbar \omega_s (A_s^\dagger A_s + \frac{1}{2}) \quad (19)$$

and the interaction Hamiltonian is

$$H_{INT} = H_{ER} + H_{EV} = \sum_{\alpha, \alpha', n} [f(n, \alpha, \alpha') a_n^\dagger c_\alpha^\dagger c_{\alpha'} + \text{complex conjugate}] \\ + \sum_{\alpha, \alpha', s} [g(s, \alpha, \alpha') A_s^\dagger c_\alpha^\dagger c_{\alpha'} + \text{complex conjugate}] \quad (20)$$

In Eqs. 18 and 19, ϵ_α is the energy of an electronic excitation on a target molecule, H_{ER} is the interaction of the photons with the electronic states of the target molecule, and H_{EV} is the interaction of the vibrational modes with the electronic states of the target molecule. The coefficient $f(n, \alpha, \alpha')$ (the matrix element of the electron/electromagnetic-field interaction, $e \frac{\mathbf{p} \cdot \mathbf{A}}{c}$) is

$$f(n, \alpha, \alpha') = \sqrt{\frac{e^2 \hbar^2}{2 \omega n^2 c^2}} \int d^3x u(x) \psi^\dagger(x) \mathbf{p} \psi(x) \quad (21)$$

From Equation 4, $u(x)$ is seen to vary as $e^{ik_1 x} e^{-k_2 x}$ so that, in the dipole approximation,

$$f_{EVANESCENT}(n, \alpha, \alpha') = \sqrt{\frac{e^2 \hbar^2}{2 \omega n^2 c^2}} e^{-k_2 x} \int d^3x \psi^\dagger(x) \mathbf{p} \psi(x) = e^{-k_2 x} f_{PLANE WAVE}(n, \alpha, \alpha') \quad (22)$$

The important thing to note is that, in the Hamiltonian (Eqs. 19 and 20), it is only in the coefficient $f(n, \alpha, \alpha')$ that a difference exists between evanescent-field Raman scattering and bulk Raman scattering.⁶ Additionally, since the analysis here is concerned with determining the intensity of Raman-scattered photons which are trapped in the fiber, a sensible approximation is to address the forward scattering only.

Birman applies a canonical transformation method to Eqs. 19 and 20 to derive the intensity of Raman scattering. The result is second-order in the coefficient $f(n, \alpha, \alpha')$. Thus, if we write the polarization-averaged Raman intensity as

$$(I_{RAMAN})_{ij} = \frac{\omega_0^4 \alpha_{ij} E^2}{2 \pi c^2} \quad (22)$$

⁵ J. L. Birman, *Theory of Crystal Space Groups and Lattice Dynamics*, Springer-Verlag, 1984.

⁶ The photons are, of course, different.

where i and j are the incident and observation cartesian indices, then

$$\alpha_{11\text{EVANESCENT}} = e^{-2\kappa z} \alpha_{11\text{PLANE WAVE}} \quad (23)$$

This is a reasonable result. The fiber modes are mostly plane-wave in character; a factor of $e^{-\kappa z}$ enters for the evanescent-field virtual absorption; a second factor of $e^{-\kappa z}$ enters for the virtual reemission. Within the picture adopted here, all the other physics is the same for the plane-wave and evanescent-field situations.

This analysis relates the interaction of a single Raman-active molecule with a plane wave to that of a single Raman-active molecule in the evanescent-field of a guided plane wave. To evaluate sensitivity of the proposed sensor, the effect of an ensemble of Raman-active molecules on guided waves has to be incorporated into a predictive model. This analysis provides the basis for that model. An order-of-magnitude estimate for the relative size of the evanescent-field Raman signal, compared to that for the Raman signal of a bulk sample of the same concentration, follows that for the absorption above. The Raman signal per centimeter of fiber will be on the order of one-half to one percent of that for a bulk sample of the same concentration, provided that the numerical aperture of the fiber is sufficiently greater than that of the spectrometer on which the measurement is being performed.

DISCUSSION

The above derivations are intended to provide a set of tools with which to make design predictions for large-area chemical sensors. The theoretical relationships derived herein allow us to use bulk absorption parameters and bulk Raman coefficients to understand and predict how optical interrogation will operate. These bulk parameters can easily be obtained from the literature or be measured. It will be easier and more precise to use the predictive capability than to use an experimental approach to such questions as

- What is the optimal sensor length?
- What is the optimal cross-sectional profile for the cladding?
 - How thick should the cladding be?
 - Where should the selective material be? (Is all the real action in a small region of the cladding?)
 - How much selective material should there be?
- What is the ultimate sensitivity to the target analyte?

When taken together with gas-phase diffusion theory, the theory developed herein will, in addition, provide information on the response time to be expected and similar quantities.

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