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Electric field standing wave effects in internal reflection and ATR spectroscopy

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ABSTRACT

We investigate electric field standing wave effects in the system semiinfinite incidence medium with high index of refraction/layer/vacuum, the latter being the semiinfinite exit medium. If the layer has a lower index of refraction than the incidence medium, then very strong resonances occur between the two critical angles of the system defined by the systems incidence medium/layer and incidence medium/vacuum, as the layer is then a cavity. In particular close to the lower critical angles, the evanescent fields extend strongly into the exit medium. Based on this effect we suggest two new spectroscopic modalities, namely interference-enhanced internal reflection Raman spectroscopy and interference-enhanced attenuated total reflection infrared spectroscopy.

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1. Introduction

Electric field standing wave effects play an important role in vibrational spectroscopy, i.e. in both Raman as well as in infrared spectroscopy. On the one hand, the corresponding effects may prevent spectra from a straightforward interpretation as they tend to introduce e.g. deviations from the (Bouguer)-Beer-Lambert law in infrared spectroscopy by enhancing and decreasing the electric field intensity in dependence of the wavenumber [1–12]. This means that at certain positions in the spectra absorption can be strengthened and at others weakened, which leads to oscillations of the peak intensity with the thickness of the layer and corresponding changes of the band intensity ratios. These oscillations are accompanied by changes in the band positions, making the interpretation of spectra of layered materials sometimes challenging [8,10–12]. These effects are weak in films whose refractive index is similar to that of the substrate, but they increase with the mismatch and are especially strong in films on highly-reflecting dielectric and, in particular, on metallic substrates. In case of the latter there are also indications that Raman spectra are affected by the electric field standing wave effects [13]. While interference effects can complicate the interpretation of spectra, they can also be used to enhance the signals of weak absorbers or scatterers. For the latter, this effect is called "interference-enhanced Raman scattering", which leads to enhancements that in a first approximation scale with the electric field to the power of four, $\sim E^4$, and reach factors of up to 80 [14,15]. Taking into account, that this enhancement is at disposal over the whole area of a substrate, the compared to plasmonic enhancements low enhancement factor is somewhat compensated. In infrared spectroscopy, the corresponding technique is called BML-IRRAS (buried metal layer infrared reflection absorption spectroscopy) and compares even more favorably to its plasmonic counterpart as absorption is a one-photon process and scales with the electric field squared, $\sim E^2$ [16]. In particular for the spectroscopic characterization of monolayers, the application of BML-IRRAS is preferable in many circumstances to SEIRS (surface-enhanced infrared spectroscopy). Furthermore, the preparation of the substrate is much simpler, since only a layer of appropriate thickness and refractive index has to be deposited on a metal. In addition, the enhancement factor only slowly decreases away from the spectral maximum in contrast to that for plasmonic enhancement, at least in case of resonant enhancement [17]. Despite all these advantages it must be stated that at the maximum only an enhancement of the electric field of a factor of 2 is available, and this would require a perfectly reflective metal.

In contrast to transmission and reflection, internal reflection, which is characterized by an incidence medium of higher refractive index than the exit medium (which is usually the sample), does not show the typical concomitant phenomenon of interference, namely interference fringes, which consist of periodic changes of the intensity with the wavenumber/wavelength and which are usually best visible in spectral regions without absorption [18]. In a classical setup, even if the medium in contact with the incidence medium is a layer of well-defined thickness (often the layer is directly deposited onto the incidence medium), interference effects cannot occur, as the incident electric field is either

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evanescent in the layer or attenuated by absorption. There is, however, one exception, which was so far only rarely and in a limited manner a subject of investigation [18]. In general, the layer must have a lower index of refraction than the incidence medium. If we assume that the medium below the layer is simply air or vacuum, this means that the index of refraction of the exit medium is lower than that of the layer. As a consequence, there exists a range of angles of incidence between the critical angles for the systems incidence medium/layer and incidence medium/air where interference effects can occur. The reason therefore is that if the incidence angle is not high enough to be critical for the system incidence medium/layer then there exist propagating waves inside the layer, which, however, become evanescent at the interface between layer and air. This situation persists until the critical incidence angle for the system incidence medium/layer is reached.

In the following we will show that in particular close to the critical angle for the system incidence medium/layer resonance effects of enormous extent can occur, while those close to the critical angle for the system incidence medium/air are weaker, but still much stronger than in transmission or external reflection geometries. In particular the latter effects have, as we will show, immediate potential for new kinds of enhanced spectroscopy both in infrared and in Raman spectroscopy (and potentially also in Fluorescence and UV–Vis spectroscopy), which we call *interference enhanced internal reflection and ATR spectroscopy*.

2. Theoretical Considerations

As already mentioned in the introduction, in the focus of interest in the following is the system semiinfinite incidence medium/layer/semiinfinite exit medium, where we assume that the index of refraction of the non-absorbing incidence medium n_1 is larger than that of the consecutive layer n_2 and the index of refraction of the exit medium $n_3 = 1$ (all media are assumed to be homogenous and fully characterizable by a scalar dielectric function). We will investigate this system assuming a non-zero angle of incidence α, in particular in the range between the critical angles α_{cr1} and α_{cr2}, where α_{cr1} is the critical angle for the system incidence medium/air and given by $\alpha_{cr1} = \arcsin(n_3/n_1)$ and α_{cr2} is the critical angle for the system incidence medium/layer and characterized by $\alpha_{cr2} = \arcsin(n_2/n_1)$. The reflection in this system can be calculated according to [19]

$$r = \frac{r_{j12} + r_{j23}\ \exp(2i\phi)}{1 + r_{j12} r_{j23}\ \exp(2i\phi)}, \quad j = s, p. \tag{1}$$

ϕ is the phase given by $\phi = k_{2z} d = \frac{2\pi d}{\lambda}\sqrt{n_2^2 - n_1^2\ \sin^2\alpha}$ with λ the wavelength and d the thickness of the layer.

The reflection coefficients r_{12} and r_{23} for the reflections arising from the interfaces between incidence medium (medium 1) and layer (medium 2) and layer and exit medium (medium 3) are different for perpendicular (s-) and parallel (p-) to the plane of incidence polarized light. Accordingly, they can be expressed as: [19]

$$\begin{aligned} r_{s12} &= \frac{k_{1z} - k_{2z}}{k_{1z} + k_{2z}}, \qquad r_{s23} = \frac{k_{2z} - k_{3z}}{k_{2z} + k_{3z}}; \\ r_{p12} &= \frac{n_1^2 k_{2z} - n_2^2 k_{1z}}{n_1^2 k_{2z} + n_2^2 k_{1z}}, \qquad r_{p23} = \frac{n_2^2 k_{3z} - n_3^2 k_{2z}}{n_2^2 k_{3z} + n_3^2 k_{2z}}; \\ k_{1z} &= n_1\ \cos\alpha \\ k_{iz} &= \sqrt{n_i^2 - n_1^2\ \sin^2\alpha}; \quad i = 2, 3. \end{aligned} \tag{2}$$

The overall reflectance R of the system is then given by $R = |r|^2$.

Accordingly, it is also possible to find analytical expressions for the fields in the different media. Following Yeh [19], in terms of the incoming s-polarized wave with the amplitude A the reflected field amplitude B in the incidence medium is given by:

$$B = A\frac{(k_{1z} - k_{2z})(k_{2z} + k_{3z}) + (k_{1z} + k_{2z})(k_{2z} - k_{3z})\ \exp(-2ik_{2z}d)}{(k_{1z} + k_{2z})(k_{2z} + k_{3z}) + (k_{1z} - k_{2z})(k_{2z} - k_{3z})\ \exp(-2ik_{2z}d)}. \tag{3}$$

The field inside the layer is constituted by the sum of the forward travelling wave with amplitude C and the backward travelling wave with amplitude D:

$$\begin{aligned} C &= \frac{1}{2}F\left(1 + \frac{k_{3x}}{k_{2x}}\right)\ \exp(ik_{2z}d) \\ D &= \frac{1}{2}F\left(1 - \frac{k_{3x}}{k_{2x}}\right)\ \exp(ik_{2z}d). \end{aligned} \tag{4}$$

Here, F is the amplitude of the wave travelling inside the semiinfinite exit medium which is given by:

$$F = A\frac{4k_{1z}k_{2z}\ \exp(-ik_{2z}d)}{(k_{1z} + k_{2z})(k_{2z} + k_{3z}) + (k_{1z} - k_{2z})(k_{2z} - k_{3z})\ \exp(-2ik_{2z}d)}. \tag{5}$$

For the amplitudes of the p-polarized waves analogues expressions can be found [20], which we will not reproduce here as the most interesting properties of the system above will be found for s-polarized incident radiation. Nevertheless, we will also present a few results for p-polarized radiation. To calculate the field maps of the electric field, we occasionally used home-made software solutions based on the above equations, but all field maps shown in this work have been calculated using the built-in 1D Stack Optical Solver of FDTD Solutions from Lumerical.

3. Electric Field Standing Wave Effects in Transparent Layers

For the following we assume an incidence medium with an index of refraction $n_1 = 4$ (e.g. germanium in the infrared spectral region) and for the non-absorbing layer we set $n_2 = 1.5$. Accordingly, the two critical angles $\alpha_{cr1} = \arcsin(n_3/n_1) \approx 14.48^\circ$ and $\alpha_{cr2} = \arcsin(n_2/n_1) \approx 22.02^\circ$. This means that for incidence angles $\alpha_{cr2} > \alpha > \alpha_{cr1}$ the incident electric field penetrates into the layer in form of propagating waves, while it is totally reflected at the interface between the layer and the exit medium, in which therefore only evanescent fields penetrate. Fig. 1 illustrates the situation in form of electric field maps for $\alpha = 14.5^\circ$ and compares it to that for the subcritical $\alpha = 14^\circ$ for the wavenumber range from 600 to 3200 cm^{-1}.

It is obvious from Fig. 1, but also well-known from literature [21], that for $\alpha = 14^\circ$ electric field standing waves exist due to interference at certain spectral points. This is not surprising per se, but even for this subcritical angle, the maximal field strengths are about twice as high as those that are obtainable in the system vacuum/layer/metal. Once α exceeds the critical angle α_{cr1} the maximum field strengths are again nearly doubled and the evanescent fields in medium 3 reach still deep into this medium. Generally, it seems that the electric field is less intense for p-polarization within the layer in the subcritical regime as well as above. The value for the field strength maximum is, however, with $|E_{max}| / |E_0| \approx 8$, somewhat stronger than for s-polarized light, where $|E_{max}| / |E_0| \approx 7$. With increasing angle of incidence, the extent of the evanescent fields in the direction normal to the layer stack becomes smaller and the spectral distance between the maxima increases. At the same time, the field strength at the anti-nodes increases, so that for s-polarized radiation the maximum field strength $|E_{max}| / |E_0| \approx 23.4$ at $\alpha = 21.5^\circ$ as can be seen in Fig. 2.

Close to α_{cr2} the field strengths in this system decreases (at least in the considered spectral region) and once $\alpha > \alpha_{cr2}$ the maximum field strengths $|E_{max}| / |E_0| = 2$ like in the system vacuum/layer/PEC, where PEC is a perfect electric conductor (in contrast to a PEC, however, which is the idealization of a perfect reflector, in the internal reflection system, perfect reflection is indeed realizable). The surprisingly high electric field strength should give rise to potential applications in

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