Estimation of surface density of molecules adsorbed on a whispering gallery mode resonator: Utility of isotropic polarizability

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A protocol is presented to estimate the surface density and anisotropic polarizability of molecules adsorbed on the surface of a dielectric resonator of uniform refractive index. Measurement of resonance wavelength shift of transverse electric and transverse magnetic whispering gallery modes in the resonator gives the product of the surface density and the polarizability components normal and tangential to the resonator surface. The isotropic mean of the two products is independent of the molecular orientation, allowing us to estimate the surface density with the knowledge of the isotropic polarizability. If the adsorbate consists of anisotropic molecules, one can obtain information on the orientation of the molecules from the polarizability components. We also show that the effect of dipoles induced in nearby adsorbed molecules is in practice negligible up to the highest density in random sequential adsorption.

The resonator we consider for hosting a whispering gallery mode (WGM) is a plain dielectric microsphere of radius \( a \) and refractive index \( n_1 \) suspended in another dielectric medium of RI=\( n_2 \), typically a low-RI liquid such as water. The resonance wavelength of the microsphere resonator changes from \( \lambda_0 \) to \( \lambda_0 + \Delta \lambda \) when molecules or particles having a nonzero excess polarizability adsorb onto the resonator surface. For simplicity, we assume that the shift is caused by the adsorption, and the contribution by a RI change of the surroundings is negligible. The fractional wavelength shift \( \Delta \lambda/\lambda_0 \) is proportional to the product of the excess polarizability and the surface density \( \sigma_p \) of the small adsorbate. The shift is different for transverse electric (TE) and transverse magnetic (TM) modes of WGM, as each field direction induces a different polarization in the adsorbate. In this Communication, we show that \( \sigma_p \) can be estimated from the TE and TM shifts without being compromised by the dipoles in the nearby adsorbate. Recently, TE-TM shift difference was studied in isomerization of surface-bound bacteriorhodopsin induced by short-wavelength laser light. Absorption anisotropy in total internal reflectance spectroscopy is related to the imaginary part of the polarizability.

The molecular orientation on the surface has tangential and normal components. We can assume a uniform distribution of the tangential component, but the normal component may not be random. An example is a phenol molecule anchored by its hydroxy end to silanol on a silica surface. The axis of the phenylene ring passing through one and four carbons may be tilted from the surface normal. Another example is a nonspherical protein molecule adsorbed to the surface by a tip of the molecule. We can assign the mean tangential component \( \alpha_t \) and normal component \( \alpha_n \) to the excess polarizability of the randomly oriented molecules.

The electric field of the TE mode has a tangential component only, and therefore, the mode picks up \( \alpha_t \). The fractional shift of the TE resonance caused by the adsorption is given as

\[
(\Delta \lambda/\lambda_0)_{TE} = G_{TE} \alpha_t \sigma_p/\varepsilon_0 a,
\]

where \( \varepsilon_0 \) is the vacuum permittivity and \( G_{TE} \) represents the WGM response to the adsorption and is related to electric field \( E_{TE} \) as

\[
G_{TE} = \frac{a \int \mid E_{TE} \mid^2 dA}{2 \int \varepsilon_r \mid E_{TE} \mid^2 dr},
\]

where \( \varepsilon_r = n_1^2 \) for \( r \) within the sphere and \( n_2^2 \) in the surroundings. The integrals in the denominator and the numerator are calculated for the entire space and the sphere surface, respectively. Earlier, we obtained

\[
G_{TE} = \frac{1}{n_1^2 - n_2^2}.
\]

The main component of the TM field is normal to the surface, but the tangential component cannot be neglected. The fraction of the tangential component in the intensity of evanescent field right on the sphere surface (average over the surface), \( \phi_t \), is expressed as

\[
\phi_t = \frac{1}{l(l+1)(\Gamma a)^{-2}},
\]

where the number of waves of the WGM per cycle, \( l \), can be determined from \( a \), and \( \Gamma \) is the decay rate of the evanescent field on the surface. For the first-order radial mode of WGM, \( \phi_t = (n_1^2 - n_2^2)/(2n_1^2 - n_2^2) < 1/2 \). The fractional shift of the TM mode picks up the normal component of the polarizability, \( \alpha_n \), more strongly than it does \( \alpha_t \),

\[
(\Delta \lambda/\lambda_0)_{TM} = G_{TM} \phi_t \alpha_t + (1 - \phi_t) \alpha_n \sigma_p/\varepsilon_0 a,
\]

where the response of TM resonance, \( G_{TM} \), is defined in an equation similar to Eq. (2) and is related to \( G_{TE} \) as...
\[ G_{TM} = G_{TE} \frac{(\Gamma a^2 + l(l + 1)}{(\Gamma a^2 + l(l + 1)(n_2/n_1)^2). \] (6)

From Eqs. (1) and (5), we find that the TE and TM resonance shift measurements give \( \alpha_t \) and \( \alpha_n \):

\[
\frac{\alpha_t}{e_0} = \frac{a}{G_{TE} \lambda_0} \frac{\Delta \lambda}{\lambda_0} \text{TE}. \]
(7)

\[
\frac{\alpha_n}{e_0} = \frac{a}{1 - \varphi} \frac{1}{G_{TM} \lambda_0} \frac{\Delta \lambda}{\lambda_0} \text{TM}. \]
(8)

The two anisotropic polarizabilities depend on the orientation of the adsorbed molecule. Consider, for instance, a molecule having a diagonalized polarizability tensor \( (\alpha_{xx}, \alpha_{yy}, \alpha_{zz}) \) in mutually perpendicular directions, adsorbed with the molecular \( y \) axis at angle \( \varphi \) from the normal surface and \( x \) axis parallel to the surface. Geometrical consideration gives:

\[ 2\alpha_t = 2\alpha_{xx} + \alpha_{zz} + (\alpha_{yy} - \alpha_{zz}) \sin^2 \varphi, \]
(9)

\[ \alpha_n = (\alpha_{yy} - \alpha_{zz}) \sin^2 \varphi. \]
(10)

For a simple molecule, \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz} \), and \( \alpha_{zz} \) can be evaluated using molecular orbital theory. However, \( \varphi \) is usually not known. For a large molecule, estimation of the molecular polarizabilities in the theory is not reliable. Therefore, \( \alpha_t \) and \( \alpha_n \) are not known in general. Then, the TE shift alone or TM shift alone fails to give an estimate of \( \sigma_p \). This impasse can be surmounted by taking the isotropic mean of the polarizability:

\[ \alpha_{iso} = (2\alpha_t + \alpha_n)/3, \]
(11)

which is independent of \( \varphi \).

The advantage of \( \alpha_{iso} \) is that it is related to the specific refractive index increment that can be measured:

\[ \frac{dn}{dc} = \frac{\alpha_{iso}}{2e_0\varrho_0 m_p}, \]
(12)

where \( m_p \) is the mass of the molecule or particle. Once \( \alpha_{iso} \) is determined, Eqs. (7) and (8) together with Eq. (11) give the estimate of \( \sigma_p \) and then the estimates of \( \alpha_t \) and \( \alpha_n \). The latter will provide information on the molecular orientation.

If the contribution of the surroundings’ RI change to the resonance shift is not negligible, we can subtract the contribution, since it can be estimated from the concentration of the molecules and \( dn/dc \). A better alternative is to measure the RI change of the fluid surrounding the microsphere, thus minimizing errors due to concentration uncertainties.

Here we apply the formulas [Eqs. (7), (8), and (11)] to the TE and TM shifts in adsorption of bovine serum albumin (BSA) onto an aminopropyl-modified silica microsphere we reported earlier. Since we do not have an estimate for \( dn/dc \) of BSA at the source wavelength (\( \lambda = 1.312 \mu m \)) used in the study, we adopt the value 0.182 ml/g (Ref. 10) at \( \lambda = 589 \) nm. At 1.312 \( \mu m \), the value will be slightly smaller. Use of \( n_t = 1.320 \) and \( m_p = 1.103 \times 10^{-19} \) g in Eq. (12) leads to \( \alpha_{iso}/e_0 = 53.5 \text{nm}^3 \). The reported values of 10^3 \( ka(\Delta \lambda/\lambda_0) = 7.7 \) for TE and 10.3 for TM are nearly independent of \( a \) in the range from 170 to 200 \( \mu m \). We will adopt \( a = 180 \mu m \) here. For such a sphere of \( n_2 = 1.452 \) to host a WGM at \( \lambda = 1.312 \mu m, l = 1233 \). Numerical computation of the resonance condition gives \( G_{TE} = 2.733 \), \( G_{TM} = 3.220 \), and \( \Gamma = 2.630 \text{m}^{-1} \). Then, \( \phi_0 = 0.1284 \text{ in Eq. (4).} \)

Equations (7) and (8) give \( (\alpha_t/e_0)\sigma_p = 0.588 \text{ nm and} \ (\alpha_n/e_0)\sigma_p = 0.680 \text{ nm, respectively. Therefore,} \ (\alpha_{iso}/e_0)\sigma_p = 0.619 \text{ nm. We then obtain} \ \sigma_p = 0.0117 \text{ nm}^{-1}, \ \alpha_t/e_0 = 50 \text{ nm}^2, \ \text{and} \ \alpha_n/e_0 = 58 \text{ nm}^2, \ \text{indicating the heart-shaped molecule standing on the surface. A slightly different sphere radius leads to the same values. Note that these estimates do not require assumption on the shape, size, and orientation of the adsorbed molecule, unlike our early study.} \)

In the above estimation about the surface-bound BSA, we neglected the effect of dipoles induced at nearby BSA molecules. Below we will estimate the effect on \( \alpha_{iso} \).

Earlier we considered the anisotropic dc polarizability of small spherical particles adsorbed at arbitrary densities on a planar interface of two dielectrics. When the particle diameter is sufficiently small compared with \( \lambda \), this static approximation is effective. We took into account the fields created by the dipoles induced in nearby particles as well as their mirror images across the interface. Below we show that the advantage of taking the isotropic mean of the polarizabilities extends into high surface densities. We first review the formulation briefly.

Consider two directions of the static field, tangential and normal to the surface, and of the concomitant polarization in the medium.11 The dipole \( \mu_i (i=t \text{ for tangential and} n \text{ for normal directions}) \) induced in the particle (electric permittivity \( \varepsilon_p \), radius \( R \)) immersed in medium 2 (permittivity \( \varepsilon_2 \)) is related to the field \( \mathbf{E}_{ext,i} \) in the absence of the particle in consideration and of medium 1 (permittivity \( \varepsilon_1 \)) as

\[ \mathbf{E}_{ext,i} = \mathbf{E}_{0,i}/f_i. \]
(14)

The reciprocal interference factors, \( f_n \) and \( f_t \), are expressed as

\[ f_t = 1 + \frac{\varepsilon_p - \varepsilon_2}{2(\varepsilon_p + 2\varepsilon_2)} \left( I_1 - \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} I_2 \right), \]
(15)

\[ f_n = 1 + \frac{\varepsilon_p - \varepsilon_2}{2(\varepsilon_p + 2\varepsilon_2)} \left( I_1 - \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} I_2 \right), \]
(16)

where the two integrals are defined as

\[ I_1 = \int_0^R \frac{3}{2\pi} \rho(r) r^2 \pi r dr, \]
(17)
\[ I_2 = \int_{2R}^{\infty} R^3 (8R^2 - r^2) (r^2 + 4R^2)\rho(r)2\pi r dr, \]  

(18)

with \( \rho(r) \) the density of particles at distance \( r \) from one of the particles at the interface and \( r = |\mathbf{r}| \). It was shown\(^\text{11} \) that \( -I_2/I_1 \approx 2^{-3/2} \). The exact values of \( I_1 \) and \( I_2 \) depend on the arrangement of the spherical particles on the interface. We generated many arrangements according to random sequential adsorption\(^\text{13} \) (RSA) and calculated the integrals and took the averages for different surface densities up to the highest surface density (full RSA). We also calculated \( I_1 \) and \( I_2 \) at the hexagonal close packing (hcp).

From Eqs. (13) and (14), we find that the average excess molecular polarizability \( \alpha_i \) is expressed as

\[ \alpha_i = 4\pi \varepsilon_2 R^3 \left( \frac{\varepsilon_p - \varepsilon_2}{\varepsilon_p + 2\varepsilon_2 f_i} \right). \]  

(19)

The isotropic mean of the polarizability, \( \alpha_{\text{iso}} \), is then given as

\[ \alpha_{\text{iso}} = 4\pi \varepsilon_2 R^3 \left( \frac{\varepsilon_p - \varepsilon_2}{\varepsilon_p + 2\varepsilon_2} \right)^2 \left( \frac{f_i}{f_n} \right) + \frac{1}{3} \left( \frac{\varepsilon_p - \varepsilon_2}{\varepsilon_p + 2\varepsilon_2} \right)^3 \left( \frac{f_i}{f_n} \right)^2. \]  

(20)

In the expression for the isotropic mean of the interference factors, \( (2f_i + 1/f_n)/3 \), the term linear to \( I_1 \), which gives a leading correction in Eqs. (15) and (16), is absent. Up to the second order of \( I_1 \) and \( I_2 \),

\[ \left( \frac{\varepsilon_p - \varepsilon_2}{\varepsilon_p + 2\varepsilon_2} \right)^2 \left( \frac{f_i}{f_n} \right) + \frac{1}{3} \left( \frac{\varepsilon_p - \varepsilon_2}{\varepsilon_p + 2\varepsilon_2} \right)^3 \left( \frac{f_i}{f_n} \right)^2 = \frac{1}{2} \left( \frac{\varepsilon_p - \varepsilon_2}{\varepsilon_p + 2\varepsilon_2} \right)^2 I_1^2 + \frac{1}{3} \left( \frac{\varepsilon_p - \varepsilon_2}{\varepsilon_p + 2\varepsilon_2} \right)^3 I_1 I_2. \]  

(21)

Figure 1 shows the interference factor, plotted as a function of \( n_p \), the RI of the particles, at four different area fractions \( \Phi \) of the projection of the particles onto the interface. The \( \Phi \) dependence of \( 1/f_i \) and \( 1/f_n \) is largely gone in taking their isotropic mean. At \( n_p = 1.55 \) and \( \Phi = 0.352 \), for instance, \( (2f_i + 1/f_n)/3 \approx 1.0005 \). The value increases only to 1.0016 at the full RSA (\( \Phi = 0.5469 \)). Practically speaking, the factor can be regarded as being equal to 1 at all accessible surface densities of protein adsorption. For nonspherical adsorbates, the factor \( (\varepsilon_p - \varepsilon_2)/(\varepsilon_p + 2\varepsilon_2) \) is different, but the other parts in Eqs. (15) and (16) are identical. Therefore, the extremely weak dependence of \( \alpha_{\text{iso}} \) on the surface density will be also the case. The \( \alpha_{\text{iso}} \) estimated at high densities is a good estimate of \( \alpha_{\text{iso}} \) of the isolated adsorbate. Our estimate in the preceding section for an isolated adsorbed BSA molecule does not require any correction. Note, however, that \( \alpha_i/\varepsilon_0 \) at the estimated surface density is greater than the value for the isolated molecule and \( \alpha_{\text{iso}}/\varepsilon_0 \) is smaller\(^\text{11} \).

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