signals are desired on metallic surfaces. Not only is surface damage likely, but high-power densities pose significant problems for resonant experiments,[14] such as the possibility of molecular desorption or degradation, which limits usable pulse energies to <1 (mJ/cm^2)/pulse.[11]

Further examination of data in Table I shows several predictable trends. In the low-power column, the highest signal levels were seen for doubly resonant samples (cresyl violet 670 and nile blue 690). Also, for a given molecule, higher incident powers result in higher signal levels. Note that for many molecules high-power results are not shown, reflecting laser-induced desorption or photodegradation. Desorption is particularly evident for the doubly resonant dyes and for the naphthalene derivatives, which are relatively volatile uncharged species, compared to the charged salt form of the dye molecules.

Table II shows a similar list of compounds studied with no resonances between molecular energy levels and incident frequencies. At first glance it seems surprising that high signal levels are still seen for most species. However, the high-power column in this table reflects a much higher energy density (>1 (J/cm^2)/pulse) than the high-power column of Table I. Since the observed signals are proportional to $I_1I_2|\chi^{(2)}|^2$, the high laser intensities compensate for the loss of resonant enhancement in $\chi^{(2)}$. Reflecting the common lack of resonance, detected signal levels for all samples were similar, whereas in Table I the signal levels reflected the degree of resonance. Note that no sample gave detectable signals at low incident energies, demonstrating the selectivity of the resonant experiments for mixture analysis.[7] The lack of detected signal for the nitrogen heterocycles may be due to a lack of strong orienting interactions with this surface or a very low intrinsic $\chi^{(2)}$ value.

Table III presents the resonant survey information for several metal surfaces. Note that no high-power data are presented, since pulse energy densities greater than ~5 (mJ/cm^2)/pulse damaged the metal surfaces. Signal levels observed are in all cases smaller than those on fused silica, for identical samples. This difference is inherent in the two optical geometries used, with the transmission geometry yielding signals larger than the reflection geometry signals by factors of ~5, which was verified by comparing signals for the two geometries on fused silica. The combination of the lower signal of the reflection geometry and the inability to use even medium-high powers results in the absence of detected signal for several of the nondye molecules which are observable on fused silica. Even for those samples which did give detected signals, the signals were small. For example, the signal for 1,2-naphthoquinone was at the detection limit, a factor of 10 smaller than the equivalent signal on fused silica even though both signals fall into the category denoted "+".

Finally, some nonresonant experiments on metals are listed in Table IV. Most notable here are the signals seen for pyridine and isoquinoline on silver. These experiments were actually performed on electrodes in 0.1 M KCl solution and will be described in detail elsewhere. The Ag/AgCl system has a strong $\chi^{(2)}$ signal itself.[15] At some potentials the signal is reduced with the nitrogen heterocycles present, while at other potentials the signal increases. As has been discussed in the literature, several possibilities exist in such cases.[1] One possibility is separate $\chi^{(2)}$ signals from the metal surface and the adsorbate, which can interfere with each other. A second possibility is an adsorbate-induced change in the metal surface $\chi^{(2)}$, without a separately contributing adsorbate $\chi^{(2)}$. The lack of observed $\chi^{(2)}$ signal for pyridine or isoquinoline in our resonant experiments on silver or in high-power nonresonant experiments on fused silica supports the second possibility. These species are expected to form ordered layers,[16] further suggesting that the inferred low $\chi^{(2)}$ value is based on a lack of strong resonances rather than upon orientation factors.

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Registry No. Coumarin 440, 26093-31-2; coumarin 460, 91-44-1; coumarin 480, 41267-76-9; coumarin 500, 52840-38-7; coumarin 540A, 53518-18-6; rhodamine 590, 47724-48-1; sulforhodamine 640, 60311-02-6; cresyl violet 670, 41830-80-2; nile blue 690, 53340-16-2; oxazine 725, 24796-94-9; LDS 698, 99675-01-1; 1-naphthylacetonitrile, 132-75-2; 1-nitronaphthalene, 86-57-7; 2-methoxynaphthalene, 93-04-9; 2-naphthaldehyde, 66-99-9; 1,4-naphthoquinone, 130-15-4; 1,2-naphthoquinone, 524-42-5; hydroquinone, 123-31-9; benzotriazole, 95-14-7; PBBO, 17064-47-0; BPBD 365, 79818-45-4; rhodamine 560, 13558-31-1; rhodamine 610, 64381-98-2; kiton red 620, 3520-42-1; rhodamine 640, 64339-18-0; DCM, 51325-91-8; oxazine 720, 62669-60-7; LDS 722, 92680-21-2; isoquinoline, 119-65-3; pyridine, 110-86-1; 2,6-lutidine, 108-48-5; aniline, 62-53-3; 2-hydroxypyridine, 142-08-5; 2-mercaptobenzothiazole, 149-30-4; stearic acid, 57-11-4; copper, 7440-50-8; silver, 7440-22-4; platinum, 7440-06-4; gold, 7440-57-5; aluminum, 7429-90-5; fused silica, 60676-86-0.

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Contact Angles on Chemically Heterogeneous Surfaces

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Contact angle measurements are increasingly being employed as a means of characterizing both the physical and chemical states of complex surfaces.[1-4] While the measurements themselves are straightforward enough, the common phenomenon of contact angle hysteresis has often prevented unambiguous interpretation of the results. The phenomenon is known to arise from both chemical and physical heterogeneities, i.e., from chemically distinct patches and surface roughness, and there has been much experimental and theoretical progress in our understanding of the origin of the hysteresis phenomenon.[5-9]

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Surprisingly, much less attention has been given to calculating the *equilibrium* contact angle of a chemically heterogeneous surface, for example, one composed of a mixture of hydrophobic and hydrophilic groups. As novel techniques are introduced to modify the chemical heterogeneity of surfaces,[3,4] so does the interpretation of contact angle measurements on such surfaces become increasingly more urgent. Lamb and Furlong[4] measured the contact angles of water on silica after various heat treatments, which altered the ratio of the hydrophilic silanol (Si–OH) groups to the hydrophobic siloxane (Si–O–Si) groups on the silica surfaces. They interpreted their results in terms of the phenomenological Cassie equation[10]

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \qquad (f_1 + f_2 = 1) \qquad (1)$$

which gives the contact angle θ of a liquid on a heterogeneous surface composed of a fraction f_1 of chemical groups type 1 and f_2 of groups type 2, where θ_1 and θ_2 are the contact angles on the pure homogeneous surfaces of 1 and 2, respectively. From this they inferred the equilibrium fraction or surface coverage of silanol and siloxane groups on silica heat-treated to different temperatures. Troughton et al.[3] carried out a whole range of θ measurements on surfactant-coated surfaces, employing double-chained surfactants having different end groups and chain lengths. However, they did not interpret their results in terms of any equation since they considered all present theories of wetting to be too crude in that they "do not take into account atomic-level surface microheterogeneity, especially in circumstances of the sort encountered with adsorbed thin films." The purpose of this note is to derive from first principles an equation suitable for chemically heterogeneous surfaces based on current theories of intermolecular and surface forces.

For the case of a liquid droplet on a surface, the Young–Dupré equation is

$$\gamma_L(1 + \cos\theta) = W \qquad (2)$$

where γ_L is the surface energy of the liquid and W the work of cohesion of the liquid with the surface. Thus for two homogeneous surfaces we may write

$$\gamma_L(1 + \cos\theta_1) = W_1 \qquad (3)$$

$$\gamma_L(1 + \cos\theta_2) = W_2 \qquad (4)$$

while for a heterogeneous surface made up of patches of type 1 and 2 we have

$$\gamma_L(1 + \cos\theta) = W = f_1 W_1 + f_2 W_2 \qquad (5)$$

where f_1 and f_2 are the fractional areas of the patches.

When eq 3–5 are combined we immediately obtain the Cassie equation, eq 1. Note that, in this case, it is implicitly assumed that the surface is composed of well-separated and distinct patches or domains of either type 1 or 2, so that the mean cohesion energy, W, is given by eq 5. However, if the chemical heterogeneity is not in the form of discrete patches but is of atomic or molecular dimensions, then from theories of van der Waals and electrostatic forces[11] it is clear that it is not the cohesion energy that should be averaged, but rather the polarizabilities, dipole moments, or surface charges of the surfaces. For instance, the polarizability or dipole moment of a macromolecule or system composed of different molecular or atomic moities is simply the average (arithmetic mean) of the polarizabilities or dipole moments of each component. It is this average value that must be used in the equations for calculating the van der Waals interaction energies.[11,12] (In this regard, it may also be mentioned that the concept of additivity of van der Waals forces does not apply to the interaction of condensed phases.[11])

If these quantities (i.e. polarization, dipole moment, etc.) are denoted by $\mathbf{w}_1$, $\mathbf{w}_2$, and $\mathbf{w}_L$ for the two homogeneous surfaces and the liquid, respectively, then eq 3–5 now become

$$\gamma_L(1 + \cos\theta_1) = W_1 \propto \{\mathbf{w}_1\mathbf{w}_L\}^{1/2} \qquad (6)$$

$$\gamma_L(1 + \cos\theta_2) = W_2 \propto \{\mathbf{w}_2\mathbf{w}_L\}^{1/2} \qquad (7)$$

$$\gamma_L(1 + \cos\theta) = W \propto \{(f_1\mathbf{w}_1 + f_2\mathbf{w}_2)\mathbf{w}_L\}^{1/2} \qquad (8)$$

By combining these three equations we finally arrive at a new relation:

$$(1 + \cos\theta)^2 = f_1(1 + \cos\theta_1)^2 + f_2(1 + \cos\theta_2)^2 \qquad (9)$$

which replaces the Cassie equation whenever the size of chemically heterogeneous patches approach molecular or atomic dimensions. Thus eq 9 rather than eq 1 should apply, for example, to cases such as silica surfaces on which both siloxane and silanol groups are present[4] and to surfaces coated with mixed surfactant monolayers.[3]

A comparison of eq 1 and 9 shows that, for the same values of θ_1, θ_2, f_1, and f_2, the Cassie equation will always predict a larger contact angle than that obtained from eq 9. Note, too, that as we go from molecular-sized patches to larger patches there should also be a progressive increase in the contact angle hysteresis.[5,8] For such cases eq 1 applies, where the average of θ_A and θ_R is often taken to represent the equilibrium contact angle, θ. Thus one of the predications of the present analysis is that as we go from large to small patches (while keeping θ_1, θ_2, f_1, and f_2 the same) not only should the contact angle hysteresis decrease, but the average contact angle θ itself should also decrease at the same time. However, a quantitative test of these equations must await a detailed study of contact angles on heterogeneous surfaces carried out in parallel with determinations of f_1 and f_2 using, for example, scanning tunneling microscopy (STM) or atomic force microscopy (AFM).

While the present model is somewhat primitive, it is unlikely that a more sophisticated analysis will provide as simple and general a first-approximation equation as eq 9. For more rigor, each system will probably have to be considered in terms of the specific intermolecular forces appropriate to that system.

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