The geometry factor in photoprocesses on irregular (fractal) surfaces. 1. Static considerations

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As an alternative one could suspect the presence of some impurity in which, for instance, a copper(II) ion is missing in the cluster, or to interactions between neighboring clusters in the triplet state, yielding $S = 1$ states. The second alternative might be confirmed by the presence of satellites flanking the $\Delta M = \pm 1$ transition at low temperature. Indeed similar absorptions were assigned to transitions between states generated by the interaction between neighboring molecules in the triplet state in the spectra of a copper(II) maleonitrile dithiolate analyzed by Keijzers et al.[56] The possibility of such interactions is supported by the extensive network of hydrogen bonds connecting different clusters. Since they appear clearly only in few crystal orientations we did not attempt further to characterize them.

In conclusion in the present work we have observed the EPR spectra of both a quintet and a triplet originated by the exchange interaction of four equivalent copper ions arranged on the vertices of a distorted tetrahedron of S_4 symmetry. We do not see any evidence of the spectra of the other two (degenerate) triplet states. The reason for this lies presumably in unfavorable relaxation time. In fact, the spectra of the lowest triplet shows up only below 10

K, broadening beyond detection at higher temperature. If the degenerate triplets have the same behavior, then their spectra are not observed because at high temperature, when they are populated, the relaxation is too fast, while at low temperature they are practically depopulated. The data in any case show that the relaxation in the triplets is much more effective than in the quintet state, which yields a measurable spectrum also at room temperature. Since the triplet spectra of isolated pairs of copper ions are generally well resolved also at high temperature, we suspect that the fast relaxation observed in this case is related to the presence of three states with the same spin multiplicity separated by ca. 20 cm⁻¹. It is worth noting that anomalous line-width behavior has been observed also for trinuclear copper complexes[57-59] in which two doublet states are formed by the exchange interaction.

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The Geometry Factor in Photoprocesses on Irregular (Fractal) Surfaces. 1. Static Considerations

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Abstract: Surface geometry effects on photoprocesses of adsorbates are discussed, with special emphasis on problems which originate from surface irregularities of silica. It is shown that the common practice of idealizing irregular surfaces as flat ones leads to inaccuracies in the evaluations of a variety of adsorption parameters, such as effective surface area, the area occupied by one molecule, intermolecular distances, etc. Data from a number of recent reports in surface photochemistry is reanalyzed to demonstrate the possible errors and to show that the interpretation of results may be altered if the calculations are carried out without the flat surface assumption. These literature examples are the photodimerization of cyanophenanthrene, the chemiluminescent oxidation of fatty acids, the benzophenone triplet quenching, and the excimerization process in pyrenyl-derivatized silica. Calculation procedures for the above mentioned parameters on irregular surfaces are suggested based both on classical surface-science considerations and on recent fractal considerations. Computational simulations demonstrate the effect of surface irregularities on these parameters. The replacement of the flat picture with the real irregular one reveals a number of new interesting concepts: the effective surface area for reaction (the reaction area) is smaller than the effective surface area available to the reactants; the effective surface area toward an excited state adsorbed molecule is different than the ground-state case; the distance between a large and small molecule depends on which molecule diffuses toward the other; in bimolecular reactions, not all of the smaller molecules are available at any time to the larger ones. Surface heterogeneity and environmental relaxation around an excited state are discussed in terms of geometry.

1. Introduction

Photochemistry has reached a mature stage in which studies in homogeneous solutions gradually yield to studies under the more realistic conditions of heterogeneous environments. These heterogeneous environments can be fluid and flexible (water surfaces, micelles) or solid (surfaces). In this report I concentrate on the latter.

In trying to extrapolate the knowledge which has been accumulated in homogeneous photochemistry to the heterogeneous systems, one has to take into account two parameters: the physico–chemical properties of the environment and the geometrical details of the environment. These geometrical details should be taken into account both on small molecular scales of, e.g., cage

size and on larger diffusional scales (geometrical details on these two scales need not coincide). Extrapolation of the first parameter from homogeneous to heterogeneous environment has been straightforward: for instance, much of what is known about the hydrogen bond in solution can be applied directly to solid materials which have surface moieties capable of forming this bond.[1] It is the second parameter, the geometry, which is new and which cannot be extrapolated from solution studies. Whereas in solution, the environment is spherical–symmetric, reversible, and flexible, various geometries are possible around an adsorbed molecule, and

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the flexibility necessary for, e.g., environmental relaxation around an excited state is diminished. Despite the novelty of the geometrical parameter, it could still be treated without causing any new conceptual difficulties in those special cases where the geometry is simple and well defined: flat surfaces, for which two-dimensional models apply,[2] and very regular environments such as zeolites.[3] The trouble begins, however, when one applies materials with surface geometry which are ill defined in terms of the classical Euclidean geometry. "Unfortunately", most materials belong to this class, i.e., most materials, natural or synthetic, have surfaces which are irregular, fractured, and convoluted.

Under such circumstances, the geometrical parameter becomes complex and its effects—difficult to interpret. The trend in many modern studies in surface photochemistry has been to overcome this difficulty by ignoring it. Specifically, an assumption is usually made that a flat two-dimensional picture is still valid. The aim of this report is, first, to show that the effect of complex geometries cannot be underestimated and, second, to suggest working tools for dealing with this parameter. In particular, I deal with estimating intermolecular distances, surface concentrations, the area occupied by an adsorbed molecule, and the effective surface areas toward ground-state molecules, excited ones, and intermediates, and I refer to the long debate on the origin of surface heterogeneity.

In section 3 I briefly discuss several recent studies in surface photochemistry, mostly published in this journal, in which the erroneous assumption of a flat surface was made. I shall try to show that this leads not only to inaccurate estimation of the above parameters but also to a conceptually wrong picture of the reactive physical system, and I regard the latter of greater importance than the former.

2. Surface Accessibility

A common practice in many surface photochemistry studies (section 3) for calculating intermolecular distances, diffusion rates, and areas occupied by adsorbed molecules has been to use the nitrogen BET values (or MeOH adsorption from solution). However, as shown below, except for very special cases, these values are of limited relevance for the analysis of experimental data of photochemical processes involving larger molecules. A flat surface assumption is in effect an assumption that the accessibility of the surface is the same for any size of adsorbed molecule. This is, of course, not true: For a wiggly, porous material, surface accessibility toward nitrogen is greater than the surface accessibility toward, say, pyrene, simply because the smaller molecule can probe many more of the narrow geometrical features of the surface (see Figure 1 in ref 4 for an illustration). And so one expects, and indeed gets

$$A_s \geq A_l \qquad (1)$$

for

$$A = N\sigma m \qquad (2)$$

where A is the apparent or effective surface area obtained from a monolayer value m (mol of adsorbate/g adsorbent) of a molecule with cross sectional area σ, N is Avogadro's number, and s and l are small and large adsorbates, respectively. The equality in (1) holds only for a flat surface.

A corollary of ignoring inequality (1) is the following incorrect practice used to assess the surface area, S, occupied by one molecule at a monolayer coverage

$$S_l = A_s/Nm_l \qquad \text{(incorrect)} \qquad (3)$$

where A_s is usually the N_2 BET value. Equation 3 is correct only for a flat surface. For an irregular surface (or for that matter—for a flat surface as well), the best one can do is to assume that at a monolayer coverage the molecules are packed so that

$$S_l = \sigma_l \qquad (4)$$

This is a common assumption in surface science[5,6] and is usually not a bad one: we have shown recently[7] that for alkanoic acids adsorbed on silica surface, S_l and σ_l, obtained by different methods, have exactly the same values. From eq 1–4 it is clear that for an irregular surface, the use of eq 3 leads to overestimation of S_l.

Similar arguments hold also for the overestimation of S_l at submonolayer coverage, n_l. For a flat surface one can use

$$S_l = A_s/Nn_l \qquad (5a)$$

But for a wiggly surface, only the following equation holds

$$S_l = A_l/Nn_l \qquad (5b)$$

And because $A_s > A_l$ (the inequality (1)), S_l will be overestimated for an irregular surface if eq 5a is used.

Another parameter which has been incorrectly estimated is surface concentration, C. The argument is similar: surface concentration is

$$C = n/A \ (\text{mol}/\text{m}^2) \qquad (6)$$

and the use of N_2 BET value (A_s) in the form $C_l = n_l/A_s$ is a "dilution" process.

It should be kept in mind that the degree of coverage, $\theta = n/m$, is also dependent on molecular size. Thus it is possible, for instance, to obtain the same θ for different surface concentrations

$$\theta = N n\sigma/A = N n\sigma/Nm\sigma = n/m \qquad (7)$$

If $\theta_s = \theta_l$ then

$$N n_s \sigma_s / A_s = N n_l \sigma_l / A_l$$

$$C_s \sigma_s = C_l \sigma_l$$

and

$$C_s = C_l(\sigma_l/\sigma_s) \qquad (8)$$

i.e., at $\theta_s = \theta_l$, $C_s > C_l$. This is true for both flat and irregular surfaces, and again it is obvious that one cannot take the N_2 BET value for θ calculations of a larger molecule. Changes in θ are directly linked to concentration changes only within the same adsorbate/surface system. It should be noted similarly that unlike solution concentration, surface concentration depends not only on the number of "dissolved" molecules but also on their size: the larger the adsorbate is, the smaller A is, and therefore for equal number of mol/g adsorbent

$$C_l < C_s$$

Consequently, for donor–acceptor interactions on surfaces, concentrations should be calculated separately for each molecule (see below).

Another method for estimation of surface concentration is in use in surface derivatization studies[8]

$$C_u \ (\text{mol}/\text{m}^2) = w/MA_{\text{BET}} \qquad (9)$$

where w is the weight of the functional group (g/g adsorbent), M is the molecular weight of that group (g/mol), and A_{BET} is the N_2 BET surface area in units of mol/(g adsorbent + g functional groups). While this correction is in the right direction, it is still too small for wiggly surfaces (section 4) and conceptually wrong—the surface area accessible to the functionalizing agent is smaller than the irrelevant N_2 BET value.

Next I discuss the question of intermolecular distances on a surface. The distances of relevance for molecular interactions are between the van der Waals edges of the σ areas occupied by each molecule, d_σ. (We have recently discussed in great detail methods

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and problems in evaluating σ^7.)

$$d_\sigma = d - 2r_\sigma \qquad (10)$$

where r_σ is the horizontal linear extent of the adsorbed molecule (e.g., for a spherical molecule, $r_\sigma = (\sigma/\pi)^{1/2}$) and d is the center-to-center distance. For low θ values one can safely assume

$$d_\sigma = d \qquad (11)$$

It should be emphasized that the only parameter of relevance for estimating d is the effective surface area A (eq 2) and not the N_2 BET value A_s. The reason is obvious: diffusional pathways can follow the features of A_1 only, and the excess surface area

$$\Delta A = A_s - A_1 \qquad (12)$$

is unavailable for the large molecule. In such cases, the effective surface area toward diffusion will be different than A.[9-11]

In its simplest form, intermolecular distance on a surface, d, is related to the surface concentration as

$$d = (NC)^{-1/2} \qquad (13)$$

And again, taking C_s (BET) instead of C_1 will cause overestimation of d.

The estimation of intermolecular distances for biomolecular processes, e.g., donor–acceptor interactions, is less obvious. I present here the associated difficulties, and in section 4 I suggest solutions. There are three possibilities: First, that the two reacting molecules are of the same size (for instance, the excimerization of pyrene[12] and the photodimerization of acenaphthylene[13]). Equation 13 cannot be used directly for this case. Whereas it is true that the static distance between the two molecules can be calculated from eq 13, the reaction can take place *only on the effective surface area for the encounter complex*, and this surface area is much smaller than the reactants surface area (the inequality (1)); therefore, we run into the problem of how to take into account the excess surface area, ΔA (eq 12).

The second case concerns the interaction between two molecules of different size, σ_s and σ_1. On a flat surface, if the intermolecular distance between an array of adsorbed acceptor is d_A, then the average distance of a donor molecule to a nearby acceptor (d_{DA}) is smaller by a factor of[14,15]

$$d_{DA} = \frac{\int_0^{d_A} 2\pi r\, dr\, r}{\int_0^{d_A} 2\pi r\, dr} = (2/3)d_A \qquad (14)$$

where r is a radius centered at the donor molecule. On an irregular surface another correction is in place. It originates from the fact that the donor and acceptor sit in different effective surface areas. Consequently, at any given time, there is a fraction, F, of small molecules that is unavailable for the larger molecules

$$F = \Delta A / A_s \qquad (15)$$

On this is further imposed the restriction of the first case, i.e., that the effective surface area for the donor–acceptor complex is even smaller.

All of these considerations must be taken into account in Stern–Volmer analyses of quenching processes on surfaces. From the above it is clear, for instance, that in the Stern–Volmer equation

$$\phi_0/\phi_q = 1 + k_q[Q] \qquad (16)$$

the reaction rate constant, k_q, will be overestimated if the quencher concentration $[Q]$ is based on A_s (BET) (ϕ—quantum yield, τ—donor life time).

The last case concerns donor–acceptor interactions between adsorbates which can operate without diffusion and through the support, e.g., Förster-type donor–acceptor electronic energy transfer. This specific problem has been treated recently by a number of authors.[9,16-20]

3. Reanalysis of Some Examples from the Published Literature

In order to illustrate the general difficulties outlined in section 2, I now bring a few examples from a number of reported studies of surface photochemistry. Possible ways to overcome the pointed difficulties will be suggested in the next section.

1. Ware, de-Mayo and their colleagues have studied intensively various aspects of surface photochemistry.[13,21] In many of their calculations the irrelevant N_2 BET value is used. Here is a typical example, taken from their study of the photodimerization of 9-cyanophenanthrene on silica for which the intermolecular distance, d, is the parameter of interest.[13] Their values are $m_1 = 1.52 \cdot 10^{-3}$ g/g SiO_2 and $A_s = 560$ m²/g. From these values they calculate the intermolecular distances at monolayer and arrive at a mean occupied area per molecules, $S_1 = 124$ Å² (eq 4) and $d = 13$ Å. These values were calculated by using A_s instead of A_1. As described in the previous section this should lead to overestimation of S_1, and, indeed, from models they obtain $\sigma_1 = 74$ Å² (and from this, $d = 9.8$ Å). The two conceptual errors are, first, not realizing that at monolayer $S_1 = \sigma_1$ (eq 4), and second, assuming that all of A_s is accessible to σ_1. Indeed, when one calculates A_1 from the experimental m_1 and σ_1 values (eq 2), one arrives at 332 m²/g, which is, as expected (the inequality (1)), smaller than $A_s = 560$ m²/g. In fact that difference 124 Å² − 74 Å² = 50 Å² is the excess area of the fine pores and irregularities that the small N_2 or MeOH can probe but not the bulky cyanonaphthalene. The intermolecular photodimerization was performed at $\theta = 0.24$ and 0.50. At least in the case of $\theta = 0.5$ we must conclude that very little diffusion, if at all, is necessary for the dimerization: Diluting by a factor of 2, increases d by a factor of $2^{1/2}$. However, because this is a *monolayer* value which is diluted, one must use eq 10, and since $d = 2r$ at monolayer

$$d_\sigma = d - 2r = 2^{1/2} \cdot 2r - 2r = 0.8r$$

i.e., a dilution of a monolayer by a factor of 2 separates the van der Waals edges by a factor of 0.8 of the molecular diameter. In our case, there are only 4 Å between one cyanonaphthalene and the next. The surface must be extremely homogeneous to conclude on diffusional dimerization over such separations.

2. A similar error was made by Adamson et al.[22] in their elegant study of surface mobility in the chemiluminescent oxidation of fatty acids adsorbed on silica. Although acknowledging that silica does "not present the smooth lattice plane" typical of crystals, the authors used exactly this assumption in their work: For calculating intermolecular distances of adsorbed palmitic acid, they used the N_2 BET value. Not only is palmitic acid of a much larger molecule than N_2, but, as shown recently,[7] the adsorption conformation of alkanoic acids on silica is not perpendicular (like in alcohols) but horizontal, reducing even further the mutual accessibility of the acid–silica system.

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3. Turro et al. recently studied triplet energy transfer from excited benzophenone to naphthalene, coadsorbed on a number of porous silicas, in order to understand the diffusional processes on the surface.[14] "For simplicity [they] treated silica surface as two dimensional ([although] the surface of silica is very irregular), and used the silica surface areas available from N_2 BET analyses." Consequently, intermolecular distances are "obtained by calculating the average surface area—assuming a flat surface". Overestimation of intermolecular distances and of rate constants by this approach has already been discussed above, not to mention clustering effects due to surface heterogeneities. It is perhaps important to mention that although the data analysis in this work of Turro et al. was presented as based on a "flat surface" photochemistry assumption, at least some of the values (e.g., the benzophenone–naphthalene separation on 95 Å silica) were calculated[15] by assuming that the silica surface is fractal with a dimension $D = 2.97$,[6] i.e., a highly irregular surface, following the procedure outlined in section 4.2.

4. Photophysical probes have been used successfully in recent years for studying the surface properties of chromatographic materials in general and reversed-phase materials in particular. The structure of the derivatizing layer has been an issue of much debate, regarding the question of whether silanols are evenly distributed on the surface (of silica)[23] or whether they are heterogeneously clustered.[24] Lochmüller and his colleagues have used the intermolecular complexation process between ground-state and excited-state pyrene (py) to investigate this problem.[25,26] This py excimerization process has been used intensively for probing heterogeneous environments.[12,21,27,28] The idea of Lochmüller et al. was to derivatize the surface of silica with a py derivative ([3-(3-pyrenyl)propyl]dimethylchlorosilane, 3PPS) at various coverages. If excimers appear, then in the absence of diffusion, this would be an indication for regions of high density of silanols. They found that whereas the py–py intermolecular distance necessary for excimerization is <5 Å, significant excimer emission was obtained at an average distance of 12 Å.[26] It was concluded that the bonded phase is represented by clusters of ligands. From the emission decay curves of monomeric 3PPS which were fitted to three lifetime exponentials and from models on flat surface[25] it was concluded that there are three distinct populations of neighboring 3PPS ligands, differing in the interligand separation. The unrealistic assumption that the silica surface is flat weakens these conclusions: First, calculations of the intermolecular distances were based on (weight corrected) N_2 BET values (eq 9). 3PPS is a very large molecule. As estimated by the authors from models, in the minimal vertical configuration (Figure 3A in ref 25) $\sigma \sim 100$ Å^2, and in the horizontal conformation (which is probably the case because of hydrogen bonds between the SiO–H and the π-electron cloud[29] of py) it is ~ 270 Å^2 (from Figure 3B in ref 25). These values are much higher than the $\sigma(N_2) = 16.2$ Å^2, i.e., the surface probed by the silylating agents must be significantly lower than the BET value. Consequently, the intermolecular distance is lower than the reported 12 Å. In section 4.5 I estimate the correct distance for this case. The second point deals with the population distribution of the interligand confor-

mations leading to excimer formation. The very wiggly surface of silica is characterized by concave and convex zones, and a whole spectrum of mutually arranged conformations between two 3PPS ligands is possible. The distinct three populations picture must be replaced by an infinite (on an Avogadro number scale) number of excimer-generating conformers. We recall that it has been clearly shown that a three-exponential fit of decay laws cannot be used as an indication for three populations.[30,31]

The "ordered" picture that Lochmüller et al. present is also with regard to the pore network: the silica is treated as a zeolitelike material with one typical pore size, and consequently it is concluded that "pore [wall-to-wall] excimer formation can be assumed to be negligible as the mean pore diameter is 4 times greater than the maximum distance between bonding sites".[25] First, on the concave walls of a cylindrical pore, wall-to-wall distance (the pore diameter) is a *maximal* distance, and shorter interligand distances are possible if the ligands are not situated along the same diameter axis. Second, the nominal pore size in silica is merely an average value in a pore diameter distribution curve which in many silicas is rather broad.[32] In such materials most of the surface area comes from pores which are much smaller than the average pore size. For instance, in silica-60 Å, 65% of the N_2 BET surface area comes from pores <10 Å![33] Consequently, most of the 3PPS ligands will be contained not in the "average pore" (93 Å) but in pores which are much smaller. It seems, therefore, that it is not possible to conclude from this set of experiments on clustering of silanols (see section 4.6).

4. Suggested Solutions

1. Effective Surface Areas toward Reactants and Excited Intermediates. The most recommended practice for the correct evaluation of the various parameters discussed in section 2 is to perform direct measurements of effective surface areas, A. For large organic molecules the procedure is usually by adsorption from solution.[34] These A values can be used directly for determination of S_1, C, θ, and d from eq 4, 5b, 6, 7, and 13, respectively.

An interesting consequence of eq 2 is that the effective surface areas with respect to the ground state and the excited state of the same molecule *are not the same*, because $\sigma \neq \sigma^*$. Typically, σ^*, the cross sectional area of an excited molecule, will be larger than that of the ground state, because of the stretching effect of the energy excess on bonds within the molecule,[35] i.e.

$$\sigma^* > \sigma; \qquad A^* < A \qquad (17)$$

This effect, however, may be overcome by changes in the adsorption conformation due to new dipole arrangement in the molecule, e.g., a flat lying molecule may change its adsorption conformation to horizontal. Elsewhere we have shown that the lifetime of the excited state (typically on the ns scale) is sufficient for relaxation movements of the adsorbate–surface complex.[36] The area difference between A and A^*, ΔA, is available only for the smaller of the two species. Since ΔA is composed of the smaller pores and surface wiggles, one does not expect that diffusion in and out of ΔA will be reversible: those small features are energy rich and once σ or σ^* enters these zones, it will not easily diffuse out.

Similar arguments apply not only for ground state–excited state isomers but for photochemical isomerizations in general. In fact, whereas the difference between σ and σ^* is usually not very large, the difference between σ (isomer 1) and σ (isomer 2) (e.g., in E–Z photoisomerizations and in photocyclizations) can amount to several tens of Å^2. Again, in photochemical reactions of the type

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$$B \rightarrow B^* \rightarrow P$$
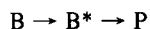
B, B*, and P, all occupy different surface areas which partially do not overlap.

Even more complex is the case of bimolecular reactions

$$Q + B \rightarrow (QB)^* \rightarrow P$$
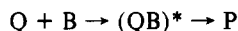
As mentioned above, the surface area of relevance is not toward Q or B but toward the largest species in this scheme, which is the excited encounter complex. Thus, whereas diffusion of A and B occurs on their respective effective surface areas, the interaction between the two can occur on a smaller surface area which is available for reaction. I call this smaller area, *the reaction area*, A_r. In the absence of better data, a good guess for σ_r would be simply $\sigma_Q + \sigma_B$. In some specific cases, where the product P is believed to be similar in structure to the encounter complex, one can assume $A_p \sim A_r$, and measure the monolayer value of P.

In summary: When a reaction is carried out in solution, the same volume is available to starting materials, intermediates, and products. By contrast, on an irregular surface the available surface area is a function of the size of the reaction components, and the smallest is the reaction area.

2. Scaling Laws in Adsorption. Although the recommended procedure for estimating A_l, the effective surface area, is to measure it, in many cases it is either impossible (intermediates) or at least difficult (rare starting materials). Recently, however, it has become possible to estimate A_l without the necessity of performing the adsorption experiment. This possibility is based on our general finding that a simple scaling law relates the size of the molecule (the yardstick, σ) to the apparent monolayer value, m,[6,7,17,28b,37,38]
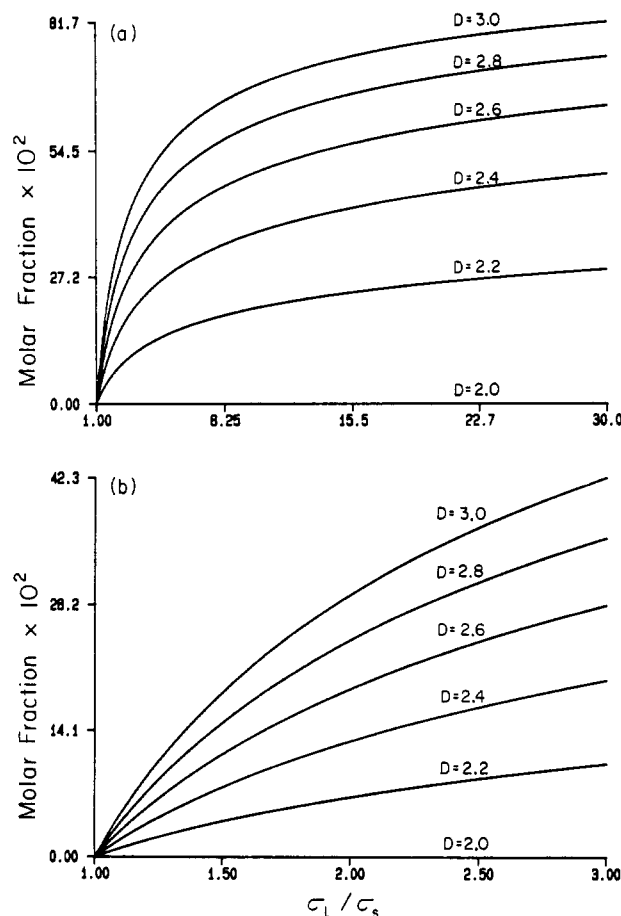
$$m = k\sigma^{-D/2} \tag{18}$$

where k is a units constant, and $D/2$ is a characteristic exponent which carries information on the degree of irregularity: it is higher the higher D is. Equation 18 indicates simply that for a given surface, fewer molecules are needed to form a monolayer, as the size of the molecule increases. And from eq 2

$$A = k\sigma^{(2-D)/2} \tag{19}$$

These simple scaling laws are fulfilled in many materials[38] including SiO_2 materials.[6,7,17,28b,38,39] Notice that D in eq 18 has two natural bounds: When $D = 2$, eq 18 becomes $m = k/\sigma$, which is the behavior one expects for a flat surface in which molecular accessibility to the surface is independent of molecular size. On the other hand, when $D = 3$, one gets $m = k\sigma^{-1.5}$ which describes volume filling. Indeed, most of the D values found are in the range $2 \leqslant D < 3$. Consequently, the best interpretation for D is that it is the surface fractal dimension. Few examples are known in which $D < 2$[38] and $D > 3$.[39] The empirical relation between m and σ is still useful in these cases.

Special attention in our fractal studies has been given to silicas, both because of the wide use of these inert supports in surface science studies and because of the ability to control the geometrical parameters. It was found in general that the average pore size (aps) and D are linked. For the nonporous silicas (Aerosil, quartz) and large pore silicas, D values are low (2.0–2.3), whereas for the narrow pore silicas (aps 40 and 60 Å) of the type used in all studies mentioned above, the D values are high (2.8–3.0). These fractal dimensions were obtained by a number of techniques.[6,17,28b,38–40]

3. Estimation of Some Adsorption Parameters. Given the N_2 BET value (A_s), the cross sectional area of N_2 ($\sigma_s = 16.2$ Å^2) and σ_l of the investigated molecule or intermediate, and the D value

(37) For short reviews, see: Avnir, D. in ref 28e, p 321. Pfeifer, P. *Chimia* **1985**, *39*, 120.

(38) (a) Avnir, D.; Pfeifer, P. *Nouv. J. Chim.* **1983**, *71*, 7. (b) Avnir, D.; Farin, D.; Pfeifer, P. *Nature (London)* **1984**, *308*, 261. (c) Avnir, D.; Farin, D.; Pfeifer, P. *J. Coll. Interface Sci.* **1985**, *103*, 112. (d) Silverberg, M.; Farin, D.; Ben-Shaul, A.; Avnir, D. *Ann. Israel Phys. Soc.* **1986**, *8*, 451, 549, 553.

(39) (a) Drake, J. M.; Klafter, J.; Dozier, W., in ref 28e. (b) Drake, J. M.; Klafter, J.; Levitz, P., in ref 40.

(40) Schmidt, P. W.; Neuman, H.-B.; Hohr, A. *Extended Abstract, Symp. Fractal Aspects of Materials*, Schaefer, D. W. et al., Eds.; Materials Research Society Meeting, Boston, Dec 1986.

(41) Alexander, S.; Orbach, R. *J. Phys. Lett.* **1982**, *43*, 2625.

Figure 1. The molar fraction, F, of small molecules of cross sectional area σ_s which are hidden from a larger molecule, σ_l, in the excess surface $\Delta A = A_s - A_l$, as a function of the ratio σ_l/σ_s, for a number of surface fractal dimensions, D, and for large, (a), and small, (b), σ_l/σ_s ratios. The best hiding place is a $D = 3.0$ surface, and there is no place to hide on a $D = 2.0$ surface.

the following calculations can be performed.

The relation between A_l and A_s is (from eq 19)

$$A_l = A_s(\sigma_l/\sigma_s)^{(2-D)/2} \tag{20}$$

from which inequality (1) is immediately obtained; and (from eq 18)

$$m_l = m_s(\sigma_l/\sigma_s)^{-D/2} \tag{21}$$

The area, S_l, occupied by one molecule in a submonolayer, n_l, is (eq 5b)

$$S_l = (A_s/Nn_l)(\sigma_l/\sigma_s)^{(2-D)/2} \tag{22}$$

Under monolayer conditions ($m_l = n_l$ in eq 22)

$$S_l = \sigma_l \tag{4}$$

(It is clear now why a flat surface assumption, eq 5a, leads to an overestimation of S_l). Similarly, eq 20 should be used for calculation of surface concentrations (eq 6, 7, and 9) and surface coverages (eq 8).

Intermolecular distances between same molecules are (eq 6, 13, and 20)

$$d = \left(\frac{A_s}{nN}\right)^{1/2}\left(\frac{\sigma_l}{\sigma_s}\right)^{(2-D)/4} \tag{23}$$

or with the corrections of eq 10.

For a bimolecular reaction, the fraction, F, of n_S mol that is hidden in ΔA is given by (eq 15 and 20)

$$F = \frac{\Delta A}{A_s} = 1 - \left(\frac{\sigma_l}{\sigma_s}\right)^{(2-D)/2} \tag{24}$$

Notice immediately that on a flat surface ($D = 2$) all is exposed and that the "best hiding place" is a $D = 3$ surface. See Figure 1 for a demonstration of the effect D has on how much n_S is unavailable. (I do not treat the more subtle picture in which proper weight is given to small molecules which sit in ΔA but "sprout" sufficiently to react with large ones. This "sprouting" property becomes more pronounced, the lower D is).

The question of intermolecular distance, d_{sl}, between a small, s, and large, l, molecule, is more complex. We first recall that the static distance and the diffusive distance between two molecules on an irregular surface do not necessarily coincide. Whereas the *static distance between two points on a fractal object is a function of D*, a diffusive pathway between these points is not only a function of D but also of the geometrical details of the connectivity between these points (the spectral dimension[9,41]) and of the energy profile of the surface.[9-11] Here I discuss the problem of static distance. Let us consider a situation where the acceptor (s) is smaller than the donor (l). A certain fraction of acceptors is unavailable at any time to the donors (eq 24), and, therefore, the effective concentration of the acceptors is smaller. This "dilution" effect results in larger d_{sl} separations (eq 13). It is on this corrected distance that the averaging procedure of eq 14 (the $^2/_3$ factor) is now performed. Notice, however, that these two correcting procedures have opposite trends and are usually of the same magnitude. If the donor is smaller than the acceptor, then all acceptors are available to the donor. In addition, one has to take into account (sections 2, 4.1) that for collisional donor–acceptor interactions, the reaction area, A_{sl}, is smaller than A_s or A_l. And so the picture is of s and l which diffuse in their effective surface areas but can react only when their diffusion pathways bring them to the smaller reaction areas. This will reduce the reaction rate in two ways: First, one has a "dilution" effect on the reactants, and, second, the diffusion rates in this reaction area are effectively reduced because part of the time the reactants are simply not there. Consequently in a diffusion-limited bimolecular reaction on an irregular surface, the reaction rate

$$v = k[s][l] \qquad (25)$$

is smaller compared to a flat surface, because of the geometry effect on the apparent k, and on the effective [s] and [l]. Whereas the effective [s], and [l] can be evaluated from eq 15, it seems to me that the only way to know k will be to measure it: there are too many factors which govern the diffusional pathways. Furthermore, the rate constant, k, may also be affected by D, since steric influences enter the prefactor in Arrhenius equation.[35]

The (static) surface distance between an s molecule and an l molecule has an interesting property—its value depends on the point of view: for an s molecule the distance is larger than for an l molecule! This property is unique to irregular surfaces and is not found in solution or gas-phase reactions. The distance, q, between two molecules of size $2r$ on an isotropic fractal object, (obtained by intersecting the object with a plane which passes through the two molecules) is[42]

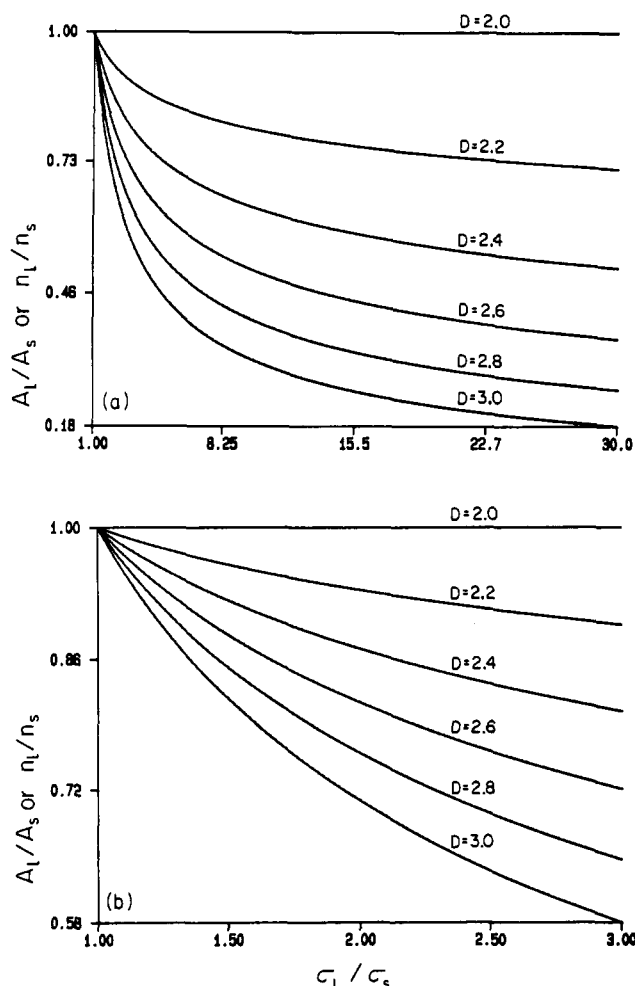$$q \propto r r^{-(D-1)} = r^{2-D} \propto \sigma^{(2-D)/2} \qquad (26)$$

and so

$$\frac{q(s \to l)}{q(l \to s)} = \left(\frac{\sigma_s}{\sigma_l}\right)^{(2-D)/2} \qquad (27)$$

(eq 26 and 19 coincide, because we have actually calculated the area of a surface strip of width $2r$).

Finally, it is important to notice that the considerations of this section are "free" of problems which arise from aggregations of adsorbates and from selection of adsorption sites which is governed by the order of addition of reactants.

4. Estimations of the Magnitude of the Effects of Surface Irregularity. I perform these estimations in two ways: First, one

(42) Mandelbrot, B. B. *The Fractal Geometry of Nature*; Freeman: San Francisco, 1982. Takayasu, H. *Fractals*; Asakura-Shoten: Tokyo, 1986.


Figure 2. The ratio of apparent surface areas, A_l/A_s, or the ratio of adsorbed moles n_l/n_s at the same surface concentration ($C_l = C_s$) as functions of molecular size ratio σ_l/σ_s for various D values and for large (a) and small (b) σ_l/σ_s ratios.

of the experimental cases described in section 3 is reanalyzed to show how fractality considerations may alter original conclusions, and, second, I present some illustrative simulations of some of the eqs of section 4.2–4.3.

Let us look again at the study of Lochmüller et al.[25,26] We recall that the main conclusion of that study was that the surface of silica is heterogeneous in the sense that it contains regions of high concentration of adsorption sites (silanols). This conclusion was based mainly on the observation that there is a sharp increase in excimer emission of bound pyrenes, at a concentration of 1.10 μmol/BET-m^2.[25] For this concentration it was calculated (by eq 9) that the intermolecular distance is 12 Å, much more than the maximal $\sim$5 Å necessary for excimerization, and since 1.1 μmol/m^2 is a "near saturation coverage", the conclusion is that there is clustering of adsorption sites. As mentioned in section 3, the "horizontal" σ of the ligand is $\sim$100 Å^2, and the σ in which the ligand can wiggle from side-to-side is $\sim$270 Å^2. From eq 13 and 19 we calculate by how much d was overestimated (d_{oe}), taking (section 4.2) $D = 3$ and $\sigma_s = 16.2$ Å^2

$$\frac{d_{oe}}{d} = \left(\frac{n_l/A_l}{n_l/A_s}\right)^{1/2} = \left(\frac{\sigma_s}{\sigma_l}\right)^{(2-D)/4} \qquad (28)$$

The d_{oe}/d ratio is close to 2 (1.8 for an average σ_l, 1.6 and 2.0 for the smaller and larger σ's), i.e., *the distance is corrected to 6–7.5 Å*. This, we recall, is the center-to-center distance. The separation between the van der Waals boundaries is still smaller (eq 10), bringing d into "touching distance".

We must conclude that the experimental data presented in ref 25 cannot be interpreted unambiguously as indicating surface heterogeneity. We also notice that in this specific case it is actually

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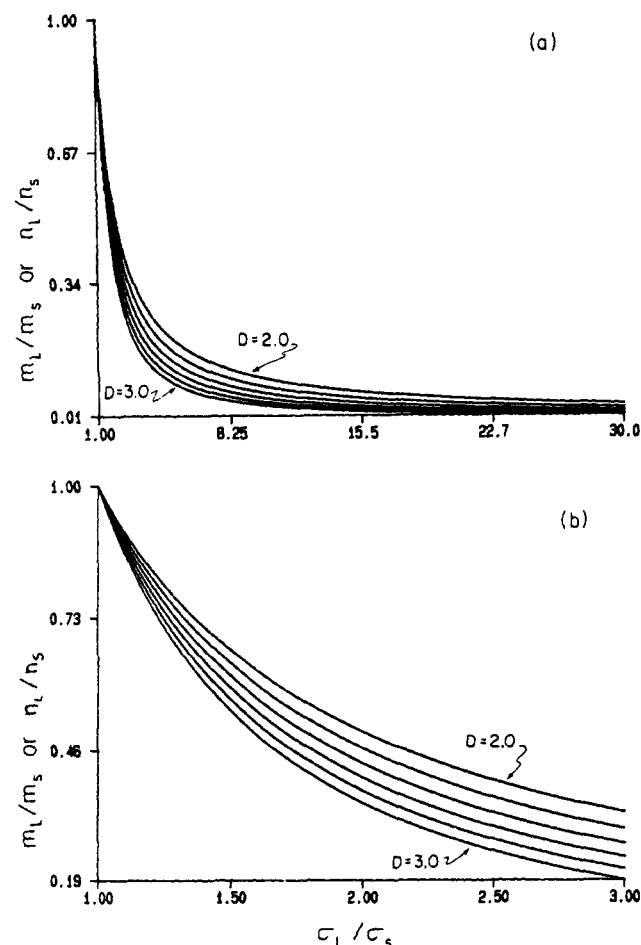
Figure 3. The ratio of monolayer values, m_1/m_s, or the ratio n_1/n_s at the same surface coverage ($\theta_1 = \theta_s$) as functions of σ_1/σ_s (large (a) and small (b) ratios) for the sequence of D values shown in Figure 2.

unnecessary to perform the above calculation: The mere statement that the 1.1 μmol/m² value is "near saturation" is equivalent to the statement that d_σ (eq 10) is zero or that $S_1 = \sigma_1$ (eq 4). I return to the heterogeneity issue in section 4.5.

An overview of the effect of D on some of the static parameters discussed above is given in Figures 2–4. First, we examine the basic property of the effect of surface irregularity on the ratio of apparent surface areas (eq 20, Figure 2). A typical case would be the N_2 BET surface area vs. the surface area as seen by an aromatic photolabile molecule. Let us take $\sigma_1/\sigma_s = 10$. Then on a $D = 2.8$ surface, only ~50% of the BET surface area is available to the organic molecule (Figure 2b). Notice that even slight irregularity ($D = 2.2$) already reduces the effective surface area by ~25%. For cases where σ_1/σ_s is not large (Figure 2a, e.g., a donor–acceptor pair), the effect is also not negligible: for, e.g., $\sigma_1/\sigma_s = 2$ on a $D = 2.6$ surface, there is a ~20% difference in surface areas. Figure 2 serves also for the following analysis: if one wishes to work under conditions where surface concentration of s and l are equal, $C_1 = C_s$, then the ratio of mol/g adsorbent is (from eq 6 and 20)

$$\frac{n_1}{n_s} = \left(\frac{\sigma_1}{\sigma_s}\right)^{(2-D)/2} \tag{29}$$

One should keep in mind that this equation cannot be used for the monolayer values, m_1 and m_s, for which always $C_1 \neq C_s$ (unless $\sigma_1 = \sigma_s$), even on a flat $D = 2.0$ surface. The changes in m_1/m_s as a function of σ_1/σ_s are (from eq 18)

$$\frac{m_1}{m_s} = \left(\frac{\sigma_1}{\sigma_s}\right)^{-D/2} \tag{30}$$

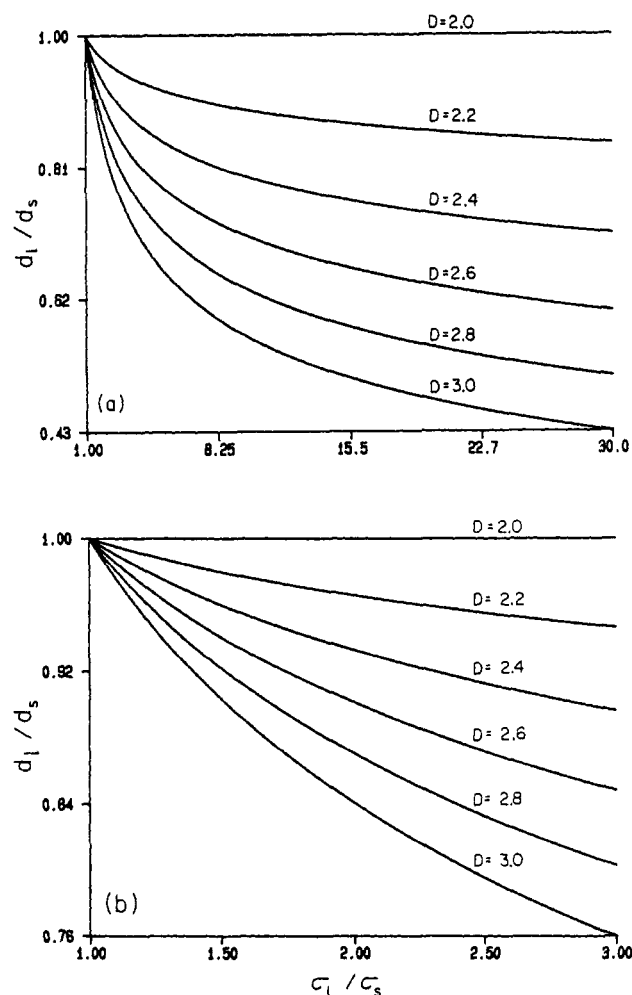One can see (Figure 3) that monolayer values are much more

Figure 4. The ratio of intermolecular distances, d_1/d_s (at $n_1 = n_s$), as a function of σ_1/σ_s.

sensitive to molecular size than apparent surface areas. The effect of D on *relative* changes in m_1/m_s is comparable to the relative changes in A_1/A_s (somewhat more sensitive). Figure 3 is also useful for the following problem: What should be n_1/n_s if one wishes to have the same surface coverage for both s and l, $\theta_s = \theta_1$? From eq 8

$$\frac{n_1}{n_s} = \left(\frac{\sigma_1}{\sigma_s}\right)^{-D/2} \tag{31}$$

A final example is the effect of molecular size on intermolecular distances. For the case $n_1 = n_s$ (from eq 13 and 20)

$$\frac{d_1}{d_s} = \left(\frac{\sigma_1}{\sigma_s}\right)^{(2-D)/4} \tag{32}$$

and as seen from Figure 4, the effect on distances becomes pronounced at the larger σ_1/σ_s ratios.

5. The Origin of Surface Heterogeneity. Relaxational Reorientation of Excited Adsorbates. As mentioned in sections 3 and 4.4, the question of whether or not the surface heterogeneity in silica originates from clustering of silanols has been under debate for quite some time. I now propose a picture which shows that actually there is no debate between the two views: From the chemical point of view it is difficult to visualize what could be a mechanistic source for the clustering of silanols during the polymerization synthesis of silica gel. I am unaware of any suggestions in that regard, and I see no reason for not accepting the assumption that a homogeneous distribution of (geminal, vicinal, and isolated) silanols results in the polymerization. Although it may seem that this type of argument is sufficient for favoring Unger's picture,[23] it is actually not. This argument is valid for a flat surface only. However, on an irregular surface,

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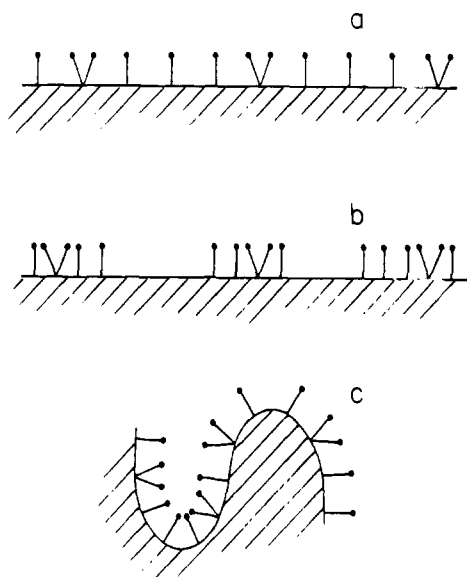
Figure 5. (a) The homogeneous view of adsorption sites of silica.[23] (b) The heterogeneous view of adsorption sites.[25] See, also Figure 2 in ref 24. (c) The suggestion of this study: a homogeneous distribution of silanols form clusters due to surface concave and convex features.

Unger and Lochmüller's pictures coincide, as is clearly evident in Figure 5: both homogeneous distribution *and* clustering describe the situation of silanols on the surface; concave zones have a high density of adsorption sites and convex zones, a smaller density. In other words, the very existence of surface irregularities and of a specific pore size distribution, and in particular the left tail of this distribution, are sufficient to account for heterogeneity of adsorption sites. I am tempted to claim that the *sole* origin of surface heterogeneity in silica is geometric in nature. This geometric picture of heterogeneity is also in keeping with known observations[43] that activity is a function of coverage. One expects

that at very low θ values the first adsorption sites to be occupied would be the very narrow pores and the highly concave surface features, which (Figure 5c) are the densest in adsorption sites; then, as θ grows, the adsorbate–adsorbent interactive system moves up the left tail of the pore distribution curve to zones which are less crowded, and surface reactions are accordingly affected. In particular I mention the environmental relaxation around an excited state. Unlike solution, in which most relaxation and resolvation movements are those of the small solvent molecules around a large solute molecule,[44] on a surface, this relaxation must be a combination of the adsorbate molecular motions together with rotations of surface groups (e.g., around an Si–OH bond). For silica-60 Å with $D \rightarrow 3.0$, on which the dual fluorescence of 1-(N,N-dimethylamino)-4-benzonitrile was studied,[36] we found that this process is extremely, almost solventlike ($D = 3.0$), efficient and is less efficient for silica-1000 Å, with $D = 2.15$.[40]

5. Summary

Environmental geometry is a primary factor in photochemical surface reactions. This parameter, which is unique to surface processes, has been overlooked in many recent surface photochemistry studies. In this report, I showed that ignoring geometrical considerations may lead to inaccuracies in the evaluation and interpretation of experimental observations. I suggested ways for correct processing of experimental data obtained from irregular surfaces. These include both classical surface science tools and the use of empirical surface science scaling laws which have been interpreted as reflecting fractal properties of the heterogeneous environment. I have shown how surface geometry affects properties such as intermolecular distances, surface concentrations, available surface for reaction and for excited intermediates, and surface heterogeneity.

(43) e.g., Al-Ekabi, H.; de Mayo, P. *J. Phys. Chem.* **1985,** *89,* 5815.

(44) Wang, Y.; Eisenthal, K. B. *J. Chem. Phys.* **1982,** *77,* 6076.

Mononuclear Oxo- and Sulfidomolybdenum(IV) Complexes: Syntheses and Crystal Structures of {HB(Me₂C₃N₂H)₃}MoE(S₂CNEt₂) (E = O, S) and Related Complexes

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Abstract: The syntheses, structures, and properties of mononuclear oxo- and sulfidomolybdenum(IV) complexes with hydrotris(3,5-dimethyl-1-pyrazolyl)borate, HB(Me₂pz)₃⁻, and dithiocarbamate ligands are described. The reactions of MoO-(S₂CNR₂)₂ (R = Me, Et, *n*-Pr, *n*-Bu) with K{HB(Me₂pz)₃} in refluxing toluene yield the green, diamagnetic, air-stable complexes {HB(Me₂pz)₃}MoO(S₂CNR₂). The complex {HB(Me₂pz)₃}MoO(S₂CNEt₂) crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.303$ (2) Å, $b = 21.710$ (4) Å, $c = 14.475$ (3) Å, $\beta = 100.75$ (2)°, $Z = 4$. The molybdenum atom is in a distorted octahedral coordination environment composed of *fac*-tridentate HB(Me₂pz)₃⁻, terminal oxo (Mo=O = 1.669 (3) Å), and bidentate S₂CNEt₂⁻ ligands. The reaction of these oxo complexes with boron sulfide in dichloromethane yields the gold-yellow, diamagnetic sulfido analogues {HB(Me₂pz)₃}MoS(S₂CNR₂). The compound {HB(Me₂pz)₃}MoS(S₂CNEt₂)·CH₂Cl₂ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 7.967$ (3) Å, $b = 14.314$ (5) Å, $c = 26.15$ (1) Å, $Z = 4$. The coordination geometry is similar to that of the oxo analogue, with Mo=S = 2.129 (2) Å.

"Oxo-type" molybdoenzymes such as sulfite oxidase, xanthine oxidase, and xanthine dehydrogenase are of considerable current

interest.[1,2] Their molybdenum centers have been probed directly by X-ray absorption spectroscopy, especially extended X-ray