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Oxidation Processes in the Gas-Phase Silane–Ozone System. Chemiluminescent Emission and the Molecular Structure of H$_2$SiO

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Abstract: The reaction of ozone with silane at low pressure in a beam-gas apparatus produces visible chemiluminescence. A portion of the emission corresponds to OH* (A$^2\Sigma^+ \rightarrow$ X$^2\pi_i$) at 310 nm. The dominant feature in the visible portion of the spectrum is thought to correspond to emission from H$_2$SiO. This assignment is based on a correlation of the observed spectral features with ab initio molecular orbital calculations on H$_2$SiO and HSiOH. The calculations were performed with a polarized double-ζ basis set at the level of configuration interaction including all single and double excitations. Calculated excitation energies are given for transitions from the X^{1}A$_1$ ground state of H$_2$SiO to the a^{3}A″ (n → π*), A^{1}A″ (n → π*), and b^{3}A′ (π → π*) excited states and from the X^{1}A′ ground state of HSiOH to the a^{3}A″ and A^{1}A″ excited states.

There has been increasing attention devoted to the study of the gas-phase reactions of silane, especially as they apply to the preparation of ultrapure semiconductor materials.[1-3] The oxidation of silane has specific application to the chemical vapor deposition of high-grade silicon oxide. Furthermore, there is a growing interest in the gas-phase oxidation of compounds containing main-group elements.[4-6] In this paper, we focus on the gas-phase reaction of ozone with silane which leads to the emission of visible and ultraviolet chemiluminescence. We also present a molecular orbital study that supports our conclusion that an important emitting species is H$_2$SiO. After completing the experimental work, we became aware of the work of Andrews and co-workers who studied the reaction of ozone with silane in a rare gas matrix.[7] These workers identified the H$_2$SiO vibrational spectrum. Prior to these current studies, only solution-phase data existed for the silane–ozone system. Spaitler et al.[8] showed that in solution an oxygen atom inserts into silane to yield silanol. The direct gas-phase production of silanol is dynamically unfavorable.

$$O_3 + SiH_4 \rightarrow H_3SiOH + O_2 \qquad (1)$$

Experimental and Computational Details. The apparatus has been described previously.[5,9] Briefly an effusive beam of ozone impinged on a tenuous atmosphere of silane (Mathieson Semiconductor Purity) in a modified beam-gas configuration. The silane pressure was kept at 30 mtorr or less.[10] The chemiluminescence was detected with a photomultiplier tube and the signals were analyzed digitally using a microcomputer-based pulse counting system. Due to low signal levels, long counting times were required.[11]

Ab initio molecular orbital calculations were done on an IBM 3083 computer using the HONDO program package.[12] Geometries were gradient optimized at the appropriate SCF level described below. Final energies were determined with configuration interaction (CI) at the level of an all single- and double-excitation CI from the appropriate valence space to the virtual space. For those points calculated on the H$_2$SiO surface, the highest five virtual orbitals corresponding to the antibonding 1s, 2s, and 2p orbitals were not included in the CI. Comparison with a CI that included all virtuals orbitals showed an error <0.001 au (0.5 kcal/mol) in total energy. For the calculations on the HSiOH portion of the surface, two virtual orbitals were excluded from the CI. Basis sets were of double-ζ plus polarization (DZ+P) quality with the form (11,7,1/9,5,1/4,1)/[6,4,1/3,2,1/2,1]; ex-

ponents and contraction coefficients were taken from Dunning and Hay.[13]

Results and Discussion

Spectra. Two of the spectra recorded in our study are shown in Figure 1. Figure 1a shows a low-resolution analog spectrum which demonstrates the range, ~300–800 nm, over which the observed broad features extend. A higher resolution (1.5 nm) spectrum, Figure 1b, shows several features that are reproducible in the wavelength range 330–630 nm. The broad-band contour was found to retain its shape for a range of reactant pressures between ~10 and 100 mtorr. Even upon the addition of 950 mtorr of Ar, no additional structure was observed. The important features in Figure 1b are at ~310, ~530, and 605 nm. The feature at 310 nm is assigned to the A$^2\Sigma^+ \rightarrow$ X$^2\pi_i$ transition of the OH radical.[14] A more detailed scan of the weak structure in the 530-nm region suggests that a portion of the chemiluminescence may be assigned to high overtone transitions between vibrational levels of the OH radical. The overtone levels are likely produced from the reaction

$$H + O_3 \rightarrow OH^\dagger + O_2 \qquad (2)$$
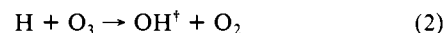
The remaining chemiluminescence including the feature at 605 nm results from transitions involving another emitter.

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(9) Glinski, R. J. Ph.D. Thesis, University of Minnesota, Minneapolis, 1983.
(10) The mechanical pump exhaust vent was purged with N$_2$ to avoid explosions at the vent.
(11) Only 150–200 Å of the spectrum could be obtained during a day's running time and the high-resolution spectrum required almost a month to obtain.
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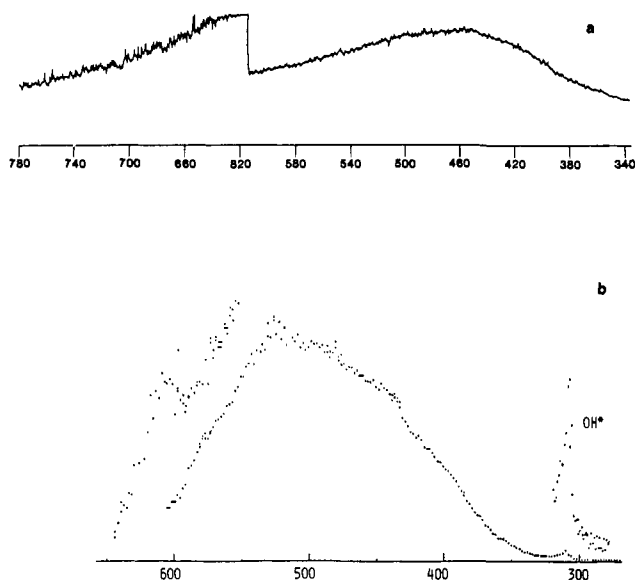
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Figure 1. Chemiluminescence spectra produced in the reaction of silane and ozone. Wavelengths in nanometers. (a) Low-resolution analog spectrum produced from the interaction of 30 mtorr of SiH_4 and 80 mtorr of O_3. The sharp peak at 620 nm corresponds to a scale change. (b) Higher resolution digital spectrum produced from the interaction of 15 mtorr of SiH_4 and 40 mtorr of O_3. The scale is also enhanced for the regions $\sim$650–$\sim$550 nm and $\sim$300 nm.
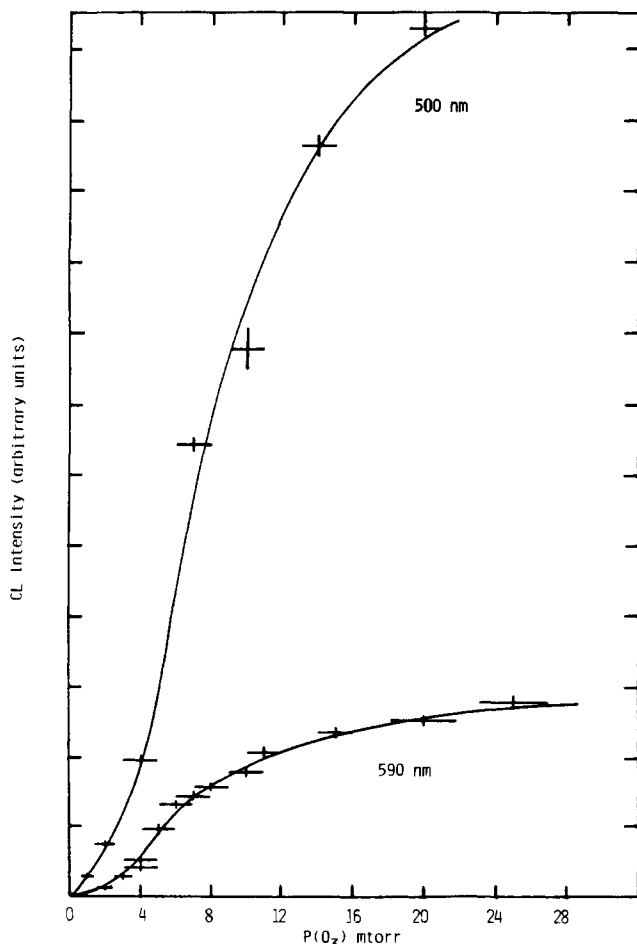
Figure 2. Dependence of the chemiluminescent intensity at 500 and 590 nm on ozone pressure at 7 mtorr of SiH_4 pressure.

Study of the emission at 500 nm indicates a linear dependence on the silane pressure. The pressure dependence $P(O_3)$, of the chemiluminescence at 500 and 590 nm is shown in Figure 2. The two curves are of the same form (their difference in intensity
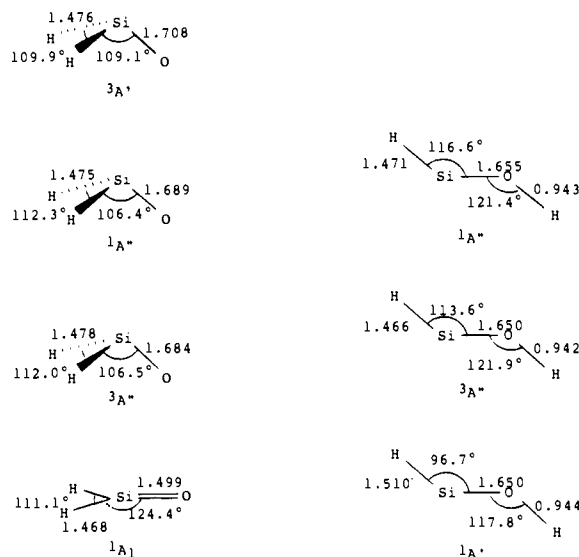

Figure 3. Calculated SCF structures with the DZ+P basis set for ground- and excited-state species of H_2SiO and HSiOH. Note that the geometry of HSiOH was determined with a two-configuration SCF wavefunction.

Table I. Relative Energies for H_2SiO and HSiOH in kcal/mol

state	SCF	CI
	H_2SiO^a	
^1A	0.0	0.0
$^3A''$	27.6	51.7
$^1A''$	30.6	56.3
$^3A''$	33.4	59.7
	$HSiOH^b$	
$^1A'$	0.0	0.0
$^3A''$	38.3	41.3
$^1A''$	82.9	77.5

^{a} Energy for H_2SiO: $-364.941\,674$ au (SCF); $-365.212\,017$ au (CI-SD). ^{b} Energy for HSiOH: $-364.973\,040$ au (two-configuration SCF); au (CI-SD).

corresponds directly to a raw data ratio). The pressure dependence is clearly second order in O_3.

The complexity of the observed emission spectrum argues for the formation of an electronically excited triatomic or larger molecule. The radicals SiH, SiH_2, and SiO all have known emission spectra that are too simple to be assigned to our complex spectrum. SiH displays well-resolved structure in the region of 405–420 nm[2,16] while the lowest energy transitions of SiO fall in the region of 285–340 nm.[17] Emission from SiH_2, observed in the region 485–650 nm, has a much more open structure.[18] Furthermore it is difficult to write a mechanism that will account for the formation of SiH_2 with sufficient electronic energy under the low collision number conditions of the present experiments.[9]

Theoretical Studies. The possible candidates giving rise to the observed emission spectrum are H_2SiO, HSiOH, or a triatomic with the stoichiometric formula (HSiO). In order to better assign the possible transitions for these species and spectral emission regions, extensive theoretical calculations have been carried out on the tetraatomics. Preliminary calculations on the HSiO radical suggest that it may be quite unstable and that the correct ground-state structure may correspond to HOSi. The ground state of H_2SiO is a planar closed-shell singlet ($^1A_1$) in exact analogy to H_2CO. The three excited states treated in our study are the a^3A'' (n → π^*), A^1A'' (n → π^*), and b^3A' (π → π^*) states. The ground state was first calculated with a closed-shell single-determinant Hartree–Fock wave function. The triplet states were determined by using the apppropriate restricted Hartree–Fock

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(17) Hager, G.; Harris, R.; Hadley, S. G. *J. Chem. Phys.* **1975**, *63*, 2810.
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wave function as was the excited singlet state. The SCF geometries for these states are depicted in Figure 3 and the appropriate excitation energies are given in Table I. We predict transitions in the wavelength regions (ignoring zero point energy differences) 5526, 5084, and 4786 Å for the a^3A'', A^1A', and b^3A' states, respectively; all of these transitions fall in the range of the observed emission feature.

The geometry of the ground state of H_2SiO is of C_{2v} symmetry. The planarity of this state was confirmed by a force-field calculation at the 3-21G level which showed no negative second derivatives and an inversion frequency of 745 cm^{-1}.[19] This is in agreement with previous calculations on H_2SiO.[20] The Si=O bond length clearly has double-bond character since a single Si—O bond length is 1.64 Å.[21] The HSiH angle is quite small. The excited-state geometries are clearly nonplanar. The HSiH bond angle is quite similar in the ground and excited states while the HSiO bond angles decrease to 106–109° in the excited states. The Si–O bond length increases by almost 0.2 Å and is 0.03–0.05 Å longer than a "normal" Si–O single bond.
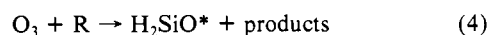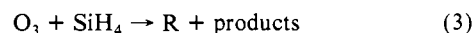
The determination of the electronic states for HSiOH is somewhat more complicated. The molecule should have an electronic structure similar to that of SiH_2 with three states important in the present study; these are the ground X^1A' state and the a^3A'' and A^1A'' excited states.[22] The A'' states have open-shell electron configurations which can be properly treated with a single electronic configuration. The ground state must be described by a two-configuration SCF wavefunction even at zero order. The structures and energies for these states are depicted in Figure 3, and indicated in Table I. Following the work of Kudo and Nagase,[23] we have only examined the trans conformation. The a^3A' ← X^1A' transition is predicted to lie in the red at ~690 nm while the A^1A' ← X^1A' transition is predicted to lie far to the blue at ~370 nm. For the similar HSiF compound, the computed transition energies (by a similar technique[22]) are slightly higher than the observed energy for the A ← X transition. Thus, our calculated transition energies may also be slightly high.

The geometries of the various HSiOH states show the behavior expected for such species. The Si–O bond length is that expected for a single bond. The HSiO bond angle is small, less than 100°, in the ground singlet state, while in the excited open-shell states, the bond angle is significantly larger. The value for r(SiH) also shows a dependence on electronic state. The bond distance is significantly longer in the ground state than in the excited states. This behavior is analogous to that observed in SiH_2.[22] The SiOH bond angle opens as expected when Si is substituted at oxygen and is about 4° larger in the excited state. Finally, we note that Kudo and Nagase[23] find H_2SiO to be 3.7 kcal/mol less stable than HSiOH (X^1A_1) whereas we find a larger energy difference, 8.0 kcal/mol.

Based primarily on our theoretical studies, we propose that the dominant chemiluminescent features in the range 4700–6500 Å correspond to H_2SiO transitions. This is the energy region where our calculations predict that the emission should be due almost completely to H_2SiO. The girth of the spectrum, the anticipated significant rotational excitation, and the lack of pronounced vibrational structure are consistent with the large increase in the Si-O bond distance (~0.2 Å) and the significant change of the HSiO angle associated with transitions from the excited states to the ground state of H_2SiO. Kudo and Nagase[23] have examined the ground-state surface for H_2SiO and HSiOH in great detail. The molecular dissociation channel to H_2 and SiO beginning at H_2SiO and proceeding through HSiOH has a barrier of 2.77 eV (2.64 eV, with ZPE effects included); this is the energy barrier for the 1,2-hydrogen shift. Thus below 4700 Å, significant predissociation of H_2SiO can occur. The presence of this pathway

can also contribute to the lack of resolvable structure in the emission spectrum and lead to a decrease in emission intensity for wavelengths below 4700 Å. Furthermore, the energy of the HSiOH $^1A''$ state is ~1 eV above the barrier for dissociation to H_2 + SiO, 2.15 eV (1.98 eV with ZPE effects), and thus may be fully predissociative, making it an even less likely candidate as the emitter for our spectrum. Thus, the quantum chemical study indicates that H_2SiO is the likely candidate for the emitter in the most intense region of the observed emission spectrum. At energies above 2.5 eV, HSiOH could also contribute to the observed emission; however, the presence of a more intense H_2SiO emission and predissociation could again obscure the vibrational structure. The fact that the spectral features do not depend on added Ar pressure suggests that the spectrum is dominated by singlet transitions since triplet transitions tend to show a larger pressure dependence. It is therefore likely that the emission emanates from the excited singlet states of H_2SiO.

Mechanism. We now propose a mechanism for the production of energy-rich H_2SiO that is consistent with the observed pressure dependence and the low collision numbers in our experiments. We wish to emphasize that this proposed mechanism is meant to be qualitative. We propose a simple three-step model involving a radical chain carrier R (the identity to be discussed later):

$$O_3 + SiH_4 \rightarrow R + \text{products} \tag{3}$$

$$O_3 + R \rightarrow H_2SiO^* + \text{products} \tag{4}$$

$$R + M \rightarrow [RM] \tag{5}$$

where (5) is a deactivation process. Solving for the intensity, I = d[H_2SiO^*]/dt, and taking a steady state in [R] we obtain

$$I = \frac{d[H_2SiO^*]}{dt} = \frac{k_3k_4[SiH][O_3]^2}{k_4[O_3] + k_5[M]} \tag{6}$$

If R is deactivated on every collision with M, for example, the wall, then $k_5[M] > k_4[O_3]$ and eq 6 reduces to

$$I = \frac{k_3k_4}{k_5[M]}[SiH_4][O_3]^2 \tag{7}$$

which is consistent with the observed pressure dependence.

We consider two possibilities for the identity of R, R = H_3SiO and R = SiH_2. If R = H_3SiO then we have an initial electrophilic attack by O_3 on silicon

$$O_3 + SiH_4 \rightarrow H_3SiO + HO_2 \tag{3a}$$
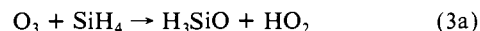
followed by hydrogen abstraction

$$O_3 + H_3SiO \rightarrow H_2SiO + OH + O_2 \tag{4a}$$
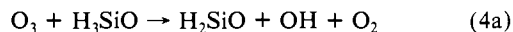
Reaction 4a is exothermic by 50–60 kcal/mol while reaction 3a is exothermic by ~30 kcal/mol.[24] This is enough energy to account for the lower energy range of the chemiluminescence, but not so large as to lead to significant predissociation. If R = SiH_2 then we have hydrogen abstraction[26]

$$O_3 + SiH_4 \rightarrow SiH_2 + H_2O + O_2 \tag{3b}$$
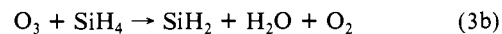
followed by oxygen abstraction by SiH_2

$$O_3 + SiH_2 \rightarrow H_2SiO + O_2 \tag{4b}$$
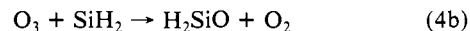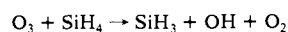
Reaction 3b is exothermic by ~42 kcal/mol while reaction 4b is very exothermic, 112 kcal/mol. This energy release is in large

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(23) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833.

(24) The heat of formation of H_3SiO is estimated as 5 kcal/mol from data in ref 25. The heat of formation of H_2SiO can be estimated from the SiO bond strength given in ref 20 as −22 kcal/mol. The remaining heats of formation are given in ref 25.
(25) (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.
(26) The abstraction of a single hydrogen atom is endothermic by ~13 kcal/mol:

$$O_3 + SiH_4 \rightarrow SiH_3 + OH + O_2$$

excess of the most energetic photon (86 kcal/mol) observed in our spectrum. The value of ΔH_{rxn} (4b) is in excess of the estimated Si–H bond strength, 85 ± 10 kcal/mol.[25] There is also enough energy to populate the A state of HSiOH. Thus if R = SiH_2 and a reasonable fraction of the exothermicity were channeled into product electronic energy, a significant amount of predissociation could occur; this is consistent with our previous discussion. The presence of two mechanisms for the generation of H_2SiO might also account for the complexity of the observed chemiluminescence.

Precipitation. Finally, we report the deposition of a white, amorphous powder on the apparatus walls resulting from the low pressure gas-phase mixture of SiH_4 and O_3. An infrared spectrum of the powder indicates features attributable to O–H and Si–O vibrational frequencies. Investigation of the IR spectrum suggests that the powder is very similar to partially hydrated silica gel (amorphous SiO_2).

Upper Excited State Reactivity and Fluorescence of Fused 8-Cyanoheptafulvenes[†]

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Abstract: Fluorescence emission of 6-cyanotricyclo[5.5.0.0²·⁵]dodeca-3,6,8,10,12-pentaene (1) is observed only from the second excited singlet states S_2 ($\phi_f = 3 \times 10^{-3}$, $\tau_f = 82$ ps) but not from S_1 in violation of Kasha's rule. Nonfused cyanoheptafulvenes are nonfluorescent due to a "free rotor effect" of the exocyclic double bond. The previously reported dependence of the photochemical valence isomerization of 1 on the excitation wavelength is, however, not due to the photoreactivity of an upper excited state but arises from "chemical" sensitization by an impurity absorbing below 320 nm.

In the course of our studies on valence isomers of nonalternant hydrocarbons,[1] we have recently reported the synthesis of 6-cyanotricyclo[5.5.0.0²·⁵]dodeca-3,6,8,10,12-pentaene (1) and its isomerization to 1-cyanoheptalene (2).[2] The present work focuses

1

2

3 (R=H)
4 (R=CN)

5
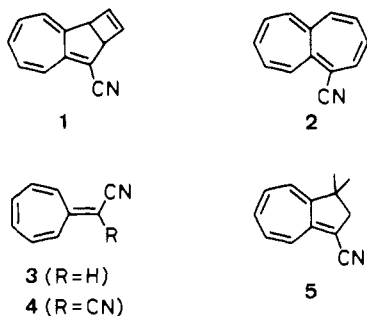
on the unusual photophysical and photochemical properties of 1, exclusive anti-Kasha fluorescence[3] from the second excited singlet state S_2 and the excitation wavelength dependence of the photoinduced valence isomerization 1 → 2. Simple rationalizations for these observations will be provided and supported by comparisons with reference compounds (3–5) and by standard PPP SCF CI[4] calculations.

Results and Discussion

Anti-Kasha Fluorescence. The fluorescence spectrum of 1 was found to be a close mirror image of the S_0–S_2 absorption band,

and the fluorescence excitation spectrum was in satisfactory agreement with the absorption spectrum below 400 nm (Figure 1). The fluorescence quantum yield, $\phi_f = 2.8 \times 10^{-3}$ (cyclohexane, room temperature), was not affected by degassing or oxygen saturation. Prolonged measurements did not produce any perceptible change in the fluorescence intensity or spectra. No fluorescence was observed to the red of the first absorption band, $\lambda > 658$ nm. PPP calculations predict that a considerable redistribution of charge is associated with S_0–S_2 excitation of the heptafulvene chromophore. This is born out by the complete loss of vibrational structure in the corresponding absorption and emission bands in polar media.

In order to exclude the remote possibility of an adventitious fluorescent impurity with these characteristics, we have determined the fluorescence lifetime of 1 by the time-correlated single-photon counting technique. The lifetime was very short, close to the time resolution of our setup. Deconvolution of the excitation pulse yielded $\tau_f = 82$ ps which may be considered as an upper limit. A calculated value of $\tau_f = 10$ ps was obtained from the relation $\tau_f = \phi_f/k_f$; this should be considered as a lower limit due to the inherent limitations of the Strickler–Berg relation[5] used to estimate k_f. We have recently obtained excellent agreement between calculated and experimental values for $\tau_f(S_2)$ in a related case,[6]

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