Time-Dependent Density Functional Theory Predictions of the Vertical Excitation Energies of Silanones as Models for the Excitation Process in Porous Silicon

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Time-dependent density functional theory calculations with a proper treatment of the asymptotic form of the exchange-correlation potential have been performed on R(R′)Si=O to predict vertical excitation energies. The species R(R′)Si=O is used as a model for the binding of the −(R)Si=O chromophore to a porous silicon surface. The calculated vertical excitation energies are substantially lower than those determined previously and show that vertical excitation of the lone chromophore is possible for all types of substituents including electronegative ones with KrF laser excitation in contrast to other predictions. If the substituents are electropositive, the chromophore can also be excited by a nitrogen laser. These results, in concert with the effect of the porous silicon surface on the R(R′)Si=O excited states, confirm our previous explanation of the photoluminescence of porous silicon as being due to the presence of Si=O chromophores and provide new insights into the photoexcitation process. The results show that the differences in the vertical and adiabatic excitation energies are strongly dependent on whether the substituents are electronegative or electropositive with the former leading to larger differences and the latter leading to smaller differences. The results for the energy differences are explained in terms of the changes in the Si=O bond length on vertical excitation and on the changes in bond angles, which are related to the ability of the Si center in the excited state to undergo an inversion process.

Introduction

Electrochemically etched highly porous silicon (PS) wafers have been the subject of great interest due to their room-temperature visible light emission observed as photoluminescence (PL) upon PL excitation (PLE) with an appropriate light source.[1−3] Whereas the PLE (absorption) spectrum of a prepared PS sample in air peaks at ∼350 nm, the resulting visible PL spectrum peaks at a considerably longer wavelength. Under the appropriate conditions, PS first displays an in situ "green" luminescence[1,2] (∼500−550 nm) during the early and intermediate stages of the etching process. The green luminescence then transforms to a final "orange-red" luminescence (600−800 nm), although it can be stabilized for extended periods with appropriate solvation.[4,5] An intense research effort over the past decade has focused on establishing the origin of the luminescence associated with the PS emitter. It is believed that the luminescence from PS occurs at or near the silicon surface. The efficiency and wavelength range of the emitted light is affected by the physical nature and electronic structure of the surface and, for in situ observations, by the nature of the etching process. However, the source of the PS luminescence is controversial. One hypothesis asserts that the luminescence results from the radiative recombination of quantum-confined electrons and holes in columnar structures or undulating wires.[6−8] Supporting evidence for this model comes from Calcott et al.[7] who reported phonon-assisted radiative processes involving those phonons

which are necessary to couple the electron valley states in crystalline silicon near the X point, to Γ-point hole states. Shuppler et al.,[9] while questioning the existence of columnar structures or undulating wires, have reported on the size, shape, and composition of luminiscent species in oxidized silicon nanocrystals, correlating their results with data on hydrogen-passivated PS and also suggesting a quantum confinement model. Such a quantum confinement model is based on localized orbitals in silicon nanoclusters on the order of 1+ nm. These excitations arise because the cluster is smaller than bulk silicon with a band gap of 1.10 eV. Therefore, the excitations are predicted to be at higher energy. A second explanation has focused on the importance of surface localized states, involving irregularly shaped small crystallites that are not perfectly passivated, wherein elementary excitations are first trapped prior to recombination.[10,11] In analogy with the well-studied luminescence from amorphous silicon (α-Si−H),[12] the carriers, in the bound states associated with reconstructed and disordered silicon in the boundary layer, are thought to recombine radiatively. A third explanation for the visible emission from porous silicon contends that the luminescence results from the presence of surface-confined molecular emitters. These include polysilane[13] formed in the internal surface of the pores or a molecular complex of silicon, oxygen, and hydrogen such as siloxane ($Si_3O_3H_6$) and its derivatives.[14] By use of the optical detection of magnetic resonance (ODMR), Stutzmann and co-workers[14] have clearly established that the PS "red" emission results from a triplet state (triplet exciton), which is thought to phosphoresce. It is the close analogy of both the ODMR and

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optical excitation (PLE) and PL spectra of PS and "annealed" siloxane that led Stutzmann and co-workers[14] to suggest this molecule as the origin of the PS photoluminescence. However, this evidence is consistent with a more general origin for the observed features in the form of the fluorophors correlated with the formation of a Si═O bond bound to the PS surface.[15] These bound fluorophors with an Si═O bond are to be distinguished from surface adsorbates.[16] In fact, Steckl et al.[17] have obtained evidence for the presence of the silicon oxyhydrides in stain-etched porous silicon thin films, correlating their observations with crystallinity and PL. Further, in a study of the thermal oxidation and nitrogen annealing of luminescent PS, Yan et al.[18] have obtained evidence that residual hydrogen exists in a 1000 °C/10 min thermally oxidized PS film, at least in the form of SiOH. In addition, Fauchet and co-workers[19] have suggested that the oxidation of H-terminated Si nanoclusters, which emit above 3.0 eV, upon oxidation, exhibit a substantial red shift and will emit in the range close to 2.0 eV. They suggest that the Si═O groups play a role in surface passivation.

On the basis of a broad set of experimental and computational results, we have demonstrated that the PL from PS is due to emission from chromophores bound to the PS surface which we concluded contain an Si═O moiety.[15,20−26] Our calculations were based on second-order Møller−Plesset calculations of the geometries of the ground-state singlet and of the excited-state triplet as well as the emission energies of small model clusters containing the Si═O moiety. The goal of this work was to model −Si(═O)R and −Si(═O)OR groups attached to a PS surface. We found that the adiabatic emission energies of the molecules containing the Si═O bond correlated with the visible spectral region and were consistent with the available experimental results.[1−5,15,20−26] But we did not rely on the energies of these model clusters in interpreting the spectra as they were basically for the chromophore and did not include all surface effects, i.e., the interaction of the electronic states of the chromophore with the bulk support states. Rather, we argued that the substantial change in the Si═O bond length, on excitation, was the main effect which affected the changes in the color of the emitting species and that these changes in the Si═O bond length were very dependent on the substituent (R, OR) group being electropositive or electronegative.[21] We did not focus on the initial excitation wavelength because much of the experimental work was done with a nitrogen laser with an excitation energy of 3.69 eV or a KrF laser with an excitation energy of 5.01 eV, and these energies correspond to wavelengths substantially far to the blue as compared to the calculated adiabatic energies.

Since our work first appeared, there have been a number of additional groups who have used computations to predict interesting behavior associated with Si nanoclusters. Zhou and Head[27] performed very similar calculations to those of Gole and Dixon[15,20−26] and concluded that silanones (directly bonded to Si atoms) are responsible for the orange-red PL from PS consistent with the predictions of Gole and Dixon. In contrast to the Gole and Dixon results, they suggest that an Si═O bonded to an OR group (an electronegative species) cannot be important because of a high vertical excitation energy associated with the Si═O chromophore excited from its ground-state geometry. They also suggest that the Si═O bond is unstable, i.e., very reactive, relative to forming Si(OH) groups based on its reactivity in the presence of H₂O. This finding is inconsistent with the experimental result[28] that a small quantity of H₂O enhances the PL, whereas further added H₂O can quench the PL from PS. The experimental work thus shows that one must add sufficient H₂O to quench the PL, thus indicating that

Si═O bonds are present when PS is formed. On the basis of UMP2 and configuration interaction singles (CIS) calculations, Zhou and Head predict that electronegative substituents will substantially raise the vertical excitation energy compared to that of the simplest model compound $H_2Si{=}O$. They calculate a vertical excitation energy of 4.33 eV for the transition from the ground-state singlet to the first triplet of $H_2Si{=}O$ at the UMP2 level, a value of 3.99 eV for this transition at the CIS level, and a value of 4.98 eV at the CIS level for the first singlet to singlet vertical excitation. For even the most electropositive substituents, SiH_3, forming $(SiH_3)_2Si{=}O$, they obtain a ground-state singlet to first triplet vertical transition energy at the UMP2 level of 3.52 eV decreasing to 3.16 eV at the CIS level and a value of 3.78 eV for the first singlet to singlet vertical excitation at the CIS level. Their calculated vertical excitation energies for electronegative substituents are substantially higher. Their conclusions are based on these calculated excitation energies, and their correlation of these results with experiments done with a nitrogen laser with an available excitation energy of 3.69 eV and a KrF laser with an excitation energy of 5.01 eV.

Work by the Galli group,[29] based on density functional theory calculations with the LDA and PBE functionals and quantum Monte Carlo calculations, suggests that the Si═O moiety can substantially alter the band gap for silicon nanoclusters up to 2 nm in size. They find that a hydrogenated Si cluster will have a band gap, defined as E(HOMO, highest-occupied molecular orbital) − E(LUMO, lowest unoccupied molecular orbital), at the LDA level below 4 eV at a cluster size with a diameter of about one nm. When oxygen is added, the band gap drops below 4 eV for all of the cluster sizes studied. They find that, when one Si═O bond is present, their calculated band gap is above the experimental results,[9,30] whereas additional oxygens lower the calculated gap. Zhou et al. have used density functional theory (DFT) with the B3LYP functional to calculate the band gap based on E(HOMO) − E(LUMO) for some Si nanoclusters terminated by hydrogen.[31] They have shown that changing the substituents on the surface of the cluster changes the orbital energies and the band gap. At the time-dependent (TD) DFT level with the Tamm−Dancoff approximation and by use of the 6-31G* basis set, they found that the singlet excitation energy is 4.47 eV for $Si_{35}H_{36}$ with a band gap defined as E(HOMO) − E(LUMO) of 5.00 eV. For $Si_{35}(OH)_{36}$, the excitation energy is 2.13 eV with a band gap of 2.73 eV. They also suggest that radical states such as R_3Si have low excitation energies around 1.0 and 3.5 eV.

In this work, we describe further calculations that provide insight into the types of excitation energies expected for Si clusters containing a Si═O bond. We provide TD-DFT and CCSD(T) results on the initial excitation energies for a number of substituted species with a Si═O chromophore, again to model the chromophore bonded to a PS surface. Our new results, while consistent with some of the trends predicted by Zhou and Head,[27] differ substantially (numerically) from their calculated values. These substantial differences completely modify the conclusions of Zhou and Head[27] in that the energies needed to excite all of the model chromophores are accessible with a KrF laser as are many with a nitrogen laser. Thus the original conclusions of Gole and Dixon[21,24] are all demonstrated to be valid as the calculated energies demonstrate that the chromophores can be excited by the laser wavelengths that were used in the experimental studies.

Calculations

The majority of the calculations described here were done with DFT. The ground-state singlet geometries were either
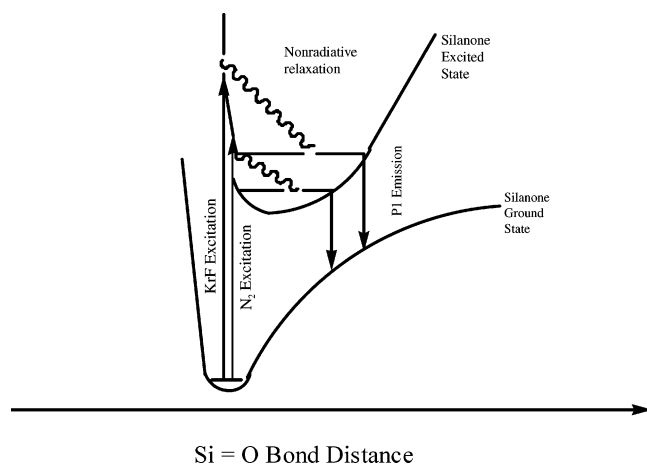
Si = O Bond Distance

Figure 1. Schematic of silicon oxyhydride ground-state singlet and excited-state potentials indicating (1) the suggested origin of the substantial difference in PLE and subsequent PL emission energies and (2) the distinction between a KrF excimer laser and nitrogen laser pump of a porous silicon sample.

obtained from our previous work or optimized at the local DFT level[32] with Slater exchange[33] and the VWN correlation functional[34] with the DZVP2 basis set.[35] Our previous studies showed little difference between the optimized geometries for the ground-state singlet obtained at the MP2 or DFT levels. Second derivative calculations showed the predicted structures to be minima. These ground-state singlet geometries were then used in TD-DFT calculations.[36,37] The TD-DFT calculations were done with the B3LYP functional[38] using the approach to correcting the long-range part of the exchange-correlation functional developed by Hirata et al.[39] following the orbital relationships developed by Zhan et al.[40] The TD-DFT calculations were done with the aug-cc-pVDZ basis set.[41] In some cases, the aug-cc-pVDZ basis set was augmented by a set of s, p, and d Rydberg functions on the O and Si atoms. These

additional functions did not affect the excitation energies by more than a few hundredths of an eV. The geometry optimizations were done with the program DGauss[42] and the TD-DFT calculations with the program NWChem.[43] Initial TD-DFT calculations with the LDA functional were done with the program Gaussian98.[44]

To calibrate our TD-DFT calculations, we calculated the energy of the ground-state singlet and the first excited-state triplet, at the singlet geometry, at the CCSD(T)/aug-cc-pVDZ level,[45] for a number of molecules with the program MOL-PRO.[46] For H_2SiO, we also did calculations at the CCSD(T) level with the aug-cc-pVTZ basis set for comparison with the smaller basis set.

Results

The vertical excitation energies for the lowest singlet−singlet transition for a number of molecular systems are summarized in Table 1. The vertical excitation for the simplest model system $H_2Si=O$, predicted to be at 3.92 eV, is forbidden and represents the HOMO−LUMO transition. CCSD(T) calculations with the aug-cc-pVDZ and aug-cc-pVTZ basis sets were used to calibrate the TD-DFT calculations. The singlet−triplet vertical transition from the optimized geometry of the ground-state singlet is predicted to be at 3.80 eV with the aug-cc-pVDZ basis set and 3.84 eV with the aug-cc-pVTZ basis set. There is little basis set dependence on the energy of this transition at the CCSD(T) level so we have used the aug-cc-pVDZ basis set in our other calibration calculations on larger molecules. Both CCSD(T) results are in reasonable agreement (within 0.3 eV) with the TD-DFT result of 3.54 eV for this transition. The adiabatic energy difference from the optimized ground-state singlet to the optimized first triplet state is 2.65 eV (Table 2). The vertical de-excitation energy from the lowest triplet state to the ground-state singlet at the optimized triplet geometry is 1.25 eV. On the ground-state singlet energy surface, the energy to distort the geometry from the optimized geometry for the singlet to

TABLE 1: TD-DFT Vertical Excitation Energies (eV) for the Singlet−Singlet Transitions

molecule	excitation energy	f[a]	assignment
$H_2Si=O$	3.92	0.00	HOMO−LUMO
	5.94	0.002	HOMO(−2)−LUMO
	6.03	0.054	NHOMO−LUMO
$H(OH)Si=O$	5.15	0.00	HOMO−LUMO
	5.92	0.039	HOMO−LUMO(+1)
$(OH)_2Si=O$	5.33	0.034	HOMO−LUMO
	5.59	0.018	NHOMO−LUMO
$(OSiH_3)_2Si=O$	5.08	0.034	HOMO−LUMO
	5.44	0.013	NHOMO−LUMO
$HSi(=O)OSi(=O)(H)$	4.68	0.002	HOMO−LUMO
	4.85	0.00	(NHOMO−LUMO) + (HOMO−LUMO(+2))
$HOSi(=O)OSi(=O)(OH)$	4.99	0.05	HOMO−LUMO
	5.05	0.003	NHOMO−LUMO
	5.32	0.029	HOMO(−2)−LUMO
	5.39	0.00	HOMO(−3)−LUMO
$H(SiH_3)Si=O$	3.30	0.001	HOMO−LUMO
	5.23	0.003	NHOMO−LUMO
$(SiH_3)_2Si=O$	2.80	0.00	HOMO−LUMO
	4.83	0.012	(HOMO−LUMO(+1)) + (HOMO−LUMO(+2))
$(SiF_3)_2Si=O$	2.89	0.00	HOMO−LUMO
	4.99	0.004	(HOMO−LUMO(+1)) + (HOMO−LUMO(+2))
	5.02	0.003	HOMO(−2)−LUMO
$(HO)(SiH_3)Si=O$	4.54	0.004	HOMO−LUMO
	5.59	0.107	HOMO−LUMO(+1)
$(SiH_3)(SiH_3O)Si=O$	4.46	0.003	HOMO−LUMO
	5.52	0.096	HOMO−LUMO(+1)
$HSi(=O)SiH_2Si(=O)H$	3.28	0.00	(HOMO−LUMO) + (NHOMO-LUMO(+1))
	3.39	0.00	(HOMO-LUMO(+1)) + (NHOMO−LUMO)

[a] Oscillator strength.

TABLE 2: Adiabatic and Vertical Lowest Energy Separations ΔE in eV for Silanones Serving as Models of PS

molecule	adiabatic		vertical		
	$\Delta E(S-T)^a$	λ(nm)	$\Delta E(S-S)^b$	λ(nm)	ΔE^c
$H_2Si=O$	2.65	468	3.92	316	1.27
$H(HO)Si=O$	3.07	403	5.15	241	2.08
$(HO)_2Si=O$	3.08	402	5.33	232	2.25
$(SiH_3)(HO)Si=O$	3.09	401	4.54	273	1.45
$H(SiH_3)Si=O$	2.48	499	3.30	375	0.82
$(SiH_3)_2Si=O$	2.34	530	2.80	443	0.46
$(SiH_3O)(SiH_3)Si=O$	3.02	411	4.46	278	1.44

^{a} $\Delta E(S-T)_{adiabatic}$ = ground-state singlet-excited triplet energy separation, for all molecules except $H_2Si=O$ calculated at the spin-projected MP2/DZP level including zero-point energy corrections. A correction factor of -4.9 kcal/mol was applied to the MP2/DZP energy splittings based on the CCSD(T)/TZ2PF calculations of $\Delta E(S-T)$ for $H_2Si=O$. The values for $\Delta E(S-S)_{adiabatic}$ are expected to be 0.1 eV higher. See text. From ref 24. ^{b} $\Delta E(S-S)_{vertical}$ = ground-state singlet-excited-state singlet energy separation. For all molecules, $\Delta E(S-S)_{vertical}$ is calculated at the TD-DFT level. ^{c} $\Delta E = \Delta E(S-S)_{vertical} - \Delta E(S-T)_{adiabatic}$.

the optimized geometry for the first triplet is 1.39 eV. Similarly, on the first triplet surface, the energy to distort the geometry from the optimized triplet geometry to the optimized ground-state singlet geometry is 1.19 eV. We note that the vertical excitation of a $Si=O$ group in the simplest model is certainly near the range of the nitrogen laser excitation energy at 3.69 eV. To provide further insight, we calculated the difference in the vertical excitation energy of the $Si=O$ bond elongated by 0.05 Å, representative of the degree of geometry excursion possible in low vibrational states of the ground-state singlet. The excitation energy is predicted to shift to the red by 0.26 eV. Thus, the inclusion of zero-point motion alone suggests that, within this model, the $Si=O$ chromophore attached as part of even the simplest PS surface molecule is accessible to excitation by a nitrogen laser.

Substitution of an electronegative OH group for the H in $H_2Si=O$ raises the excitation energy by 1.23 eV to 5.15 eV. At the CCSD(T)/aug-cc-pVDZ level, the triplet at the optimum singlet geometry is predicted to be 5.25 eV (4.74 eV at the TD-DFT level) above the ground state, a determined shift of 1.45 eV as compared to $H_2Si=O$. This result, a predicted blue shift, is consistent with the qualitative picture of Zhou and Head.[27] However, we find that our predicted energy differences are substantially different from those predicted by Zhou and Head. They predict a value of 6.56 eV at the CIS level for the first singlet−singlet vertical transition. For the first singlet−triplet vertical transition, they predict 5.88 eV at the UMP2 level and 5.45 eV at the CIS level. In addition, we predict that increasing the bond distance of the $Si=O$ bond by 0.05 Å decreases the excitation by 0.36 eV to 4.79 eV. Our calculated excitation energies show that even $H(OH)Si=O$, a model of an electronegative ligand bonded to the $Si=O$ chromophore, could be excited by a KrF laser at 5.01 eV as has been applied in many experiments which excite the porous silicon PL. Zhou and Head,[27] based on their calculated energies, strongly suggest that this is not possible.

We predict that the substitution of a second OH for H to form $(OH)_2Si=O$ raises the excitation energy to only 5.33 eV as compared to Zhou and Head's calculated values of 7.85 eV at the CIS level for the singlet and, for the triplet, 7.15 eV at the UMP2 level and 6.73 eV at the CIS level. At the CCSD-(T)/aug-cc-pVDZ level, the vertical excitation to the triplet from the singlet is 5.37 eV (4.95 eV at the TDDFT level), a small shift of 0.12 eV as compared to the vertical transition to the

triplet in $H(HO)Si=O$ at the CCSD(T) level. Again, we predict that lengthening the $Si=O$ bond by 0.05 Å leads to a decrease in the excitation energy to 5.07 eV, close to the KrF laser excitation energy. If the two OH groups are substituted by two $OSiH_3$ groups, the predicted excitation energy drops from 5.33 to 5.08 eV. Thus our computational results, obtained at a higher level, clearly demonstrate that a large excitation energy outside the range of the sources used to excite PL is not needed to excite the $Si=O$ chromophore even if it is bonded to electronegative substituents.

If electropositive groups are substituted for the H in $H_2Si=O$, we predict a substantial shift to lower vertical excitation energy, consistent with the qualitative picture presented by Zhou and Head.[27] If one of the H atoms is substituted by a SiH_3 group, the excitation energy drops to 3.30 eV. At the CCSD(T) level, the vertical transition to the triplet is 3.22 eV above the ground-state singlet (2.81 eV at the TD-DFT level), a significant red shift as compared to the CCSD(T) value of 3.80 eV for $H_2Si=O$. If two SiH_3 groups are substituted for the two H atoms in $H_2Si=O$, the vertical excitation energy drops substantially to 2.80 eV, considerably lower than the value of 3.78 eV predicted by Zhou and Head at the CIS level, and below the values of 3.52 eV at the UMP2 level and 3.16 eV at the CIS level for the triplet. At the CCSD(T) level, the calculated vertical excitation energy to the triplet is 2.68 eV (the TD-DFT values is 2.33 eV), showing a similar energy shift. If the hydrogens on the SiH_3 are substituted by fluorine atoms to form SiF_3 groups and simulate the presence of electronegative groups on the Si substituent, our predicted excitation energy increases by only ~0.1 eV to 2.89 eV. Thus, our results show that the $Si=O$ chromophore can readily be excited by the laser excitation energy from an N_2 laser when it is bonded to a Si atom. This is consistent with porous silicon that is only partially oxidized. If one of the SiH_3 groups is replaced by a OH or a $OSiH_3$ group, the excitation energy is predicted to increase to ~4.5 eV. This is consistent with the predicted changes found for H_2SiO.

We have also investigated structures with two $Si=O$ groups separated by an O or by a SiH_2 group to model the PS surface with two $Si=O$ chromophores close to each other. For the structure with two $(HO)Si(=O)-$ groups bonded to each other by a bridging O atom, the excitation energy is predicted to be 4.99 eV, slightly below that for a $(HO)Si(=O)-$ group bonded to a H. Thus, the two chromophores do not strongly interact with each other. If the $-Si(=O)H$ groups are bridged by a SiH_2 group, the excitation energy is essentially identical to the excitation of $H(SiH_3)Si(=O)$, again showing that the two chromophores do not strongly interact with each other. These results are consistent with unpublished work in one of our laboratories on models of nylon polymers. This work has shown that the amide chromophores (containing a $C=O$ group) in such a polymer only weakly interact with each other and cause only small changes in the location of spectral transitions when compared to the isolated chromophore.

As shown above, we estimate that our TD-DFT calculations underestimate the transition energy by 0.3−0.5 eV based on comparison to the CCSD(T) vertical triplet excitation energies. The TD-DFT results are a substantial improvement over the CIS results[27] where overestimations of up to 1.4 eV or higher are found as compared to the CCSD(T) results. In addition, vibrational effects (zero-point energies) could be different on the ground- and excited-state surfaces. This difference is not expected to be large and will be predominantly found in the $Si=O$ stretch. We can estimate a maximum value for this quantity based on the differences in the $Si=O$ bond stretches

for the optimized singlet and triplet. This difference is 400–450 cm^{-1}, and thus the zero-point contribution is ∼0.6 kcal/mol (∼0.03 eV). However, this difference and the errors in the TD-DFT results are comparable or smaller than the effects of coupling the surface and bulk states to the model isolated chromophore, which is expected to lower the energy of excitation for Si=O.

We have previously been able to explain the dramatic red shift in the PL vs PLE spectrum of PS by invoking a significant change in the Si–O bond distance in the excited state. The adiabatic excitation energies shown in Table 2 clearly demonstrate significant shifts from the vertical excitation energies. In Table 2, we report the adiabatic ΔE(S–T) energy differences obtained by us previously.[24] The adiabatic value for ΔE(S–S) for H_2Si=O is calculated[24] to be 2.6 kcal/mol or ∼0.1 eV higher than ΔE(S–T) so that using ΔE(S–T)$_{adiabatic}$ is a reasonable approximation for ΔE(S–S)$_{adiabatic}$. The results in this table clearly show that the structures with higher vertical excitation energies have higher adiabatic energy differences. These compounds have electronegative substituents attached to them. Thus, the values of $\Delta E = \Delta E$(S–S)$_{vertical} - \Delta E$(S–T)$_{adiabatic}$ demonstrate that the compounds with electronegative substituents show the largest difference between adiabatic and vertical excitation energies. If there are two electronegative substituents, the difference is nearly 2 eV, and with one, the difference is near 1.5 eV. However, with two H substituents, the difference is 1.3 eV. The substitution of a SiH_3 for a hydrogen leads to a lowering of 0.8 eV, whereas the presence of two electropositive substituents leads to an even smaller difference of only 0.5 eV.

The results show a large spread for the difference in the vertical and adiabatic energies. Although the difference in the "Si=O" bond length ground- and excited-state geometries for R_2Si=O is a significant 0.15–0.17 Å, this is not the only factor which affects the difference between the vertical and adiabatic transitions in the silanones, as found for $(SiH_3)_2Si$=O. We suggest that quoting absolute "vertical" and "adiabatic" energy separations tends to overshadow the broad nature of the distribution which marks the population of the ground states of the species considered in these studies and its reflection on the width of the vertical and adiabatic energy increments. In addition to considering the changes in bond lengths, one must also consider the effects of changes in the bond angles. The ground state of the silanones has an approximate trigonal planar geometry. Upon excitation, one forms an effective diradical with one electron on the Si and one on the =O. This type of structure without a π Si=O bond no longer wants to be planar as it is effectively a radical Si center with 3 ligands. As expected, it will be nonplanar as found for the optimized geometry of the triplet. Thus a measure of the difference between the "planar" ground-state singlet and the excited-state pyramidal structure is the size of the inversion barrier as the vertical excitation process leaves the molecule in the transition state for inverting the pyramidal geometry of the radical. In fact, the vertical excitation process leaves the excited-state geometry in a very specific form of the inversion transition state corresponding to vertex inversion as typified by NH_3. In a number of studies of such inversion processes, it has been shown that the barrier to vertex inversion is lowered when there are electropositive substituents and raised for electronegative species.[47–52] In fact, for molecules such as PF_3, the vertex inversion process does not occur and the inversion proceeds through a totally different mechanism known as edge inversion which leads to a planar T-shaped intermediate with the lone pair in the plane.[49] For our Si-centered tri-coordinated sites in their excited state with

electronegative ligands such as OH, OR, or O•, we would expect that the electronegative substituents would lead to a planar species, which resembles the vertex inversion transition state. This transition state is substantially higher in energy than the optimum pyramidal structure leading to its higher vertical excitation energy and to a larger value for ΔE as defined above. If the substituents are electropositive, then the vertex inversion barrier is lower. This leads to a lower vertical excitation energy and to a smaller value of ΔE. The trends that we have outlined are well established in Tables 1 and 2. In addition, because of the low electronegativity of the Si atom, H is more electronegative than Si. Hence the barriers with H should be higher than with SiH_3 as a substituent. This would lead to a higher vertical excitation energy and to a larger value of ΔE for H_2Si=O as compared to $(SiH_3)_2Si$=O, just as we have predicted.

In summary, our results obtained at a higher level of description than those of Zhou and Head[27] demonstrate that silanone, Si=O, centers can serve as the chromophore responsible for the PL from PS just as we have discussed previously.[15,20–26] This new contribution establishes, with high-level TD-DFT calculations with a reasonable treatment of the asymptotic form of the exchange-correlation potential, that the Si=O chromophore can absorb light from a nitrogen laser with certain types of atom attachments on the PS surface and it can absorb light from a KrF laser with essentially any type of atom attachment likely to be found on PS. This work is consistent with CCSD(T) calculations. The results of the calculations performed here demonstrate that Si=O chromphores should be able to absorb light in the excitation ranges previously employed experimentally. Our results show that Si=O centers directly bonded to Si can easily absorb light from a nitrogen laser excitation source and that even Si=O centers bonded to an electronegative OR species can absorb light from a KrF excitation source. While Zhou and Head,[27] based on the results of calculations at a lower level, agree that an Si=O group directly bonded to an Si facilitates the absorption of light from a nitrogen laser, they have concluded that it is unlikely that a Si=O center bonded to an electronegative site can absorb light from the standard excitation sources used in the experiments. This is in direct contrast to the present results, which clearly demonstrate that such absorptions should be possible with excitation from a KrF laser.

Our results have further consequences. Zhou and Head[27] have argued that the relatively high excitation energies that they compute for the R(HO)Si=O clusters and their vertical emission energies provide little support for the assignment[21] of the green PL from PS to a −(R)Si=O fluorophor and the orange-red PL to the −(RO)Si=O fluorophor as suggested by us from computational and experimental work.[5,15,20–26] The present calculations on model clusters clearly demonstrate significantly lower vertical excitation energies, indicate the accessibility of nitrogen and KrF laser excitation, in contrast to the conclusion of Zhou and Head[27] for compounds with electronegative substituents, and support the assignments given by Gole and Dixon.[15,20–26]

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