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Photoabsorption and photoluminescence of divalent defects in silicate and germanosilicate glasses: First-principles calculations

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The photoabsorption and photoluminescence of divalent defects in silicate and germanosilicate glasses have been studied by first-principles quantum-chemical techniques. Divalent Si and divalent Ge defects have very similar excitations. They have singlet-to-singlet excitations at 5.2 eV (Si) and 5.1 eV (Ge), and singlet-to-triplet excitations at 3.1 eV (Si) and 3.4 eV (Ge). The excited-state geometries have been relaxed to obtain the corresponding photoluminescence energies. Singlet-to-singlet luminescence transitions occur at 4.5 eV (Si) and 4.1 eV (Ge), and triplet-to-singlet transitions occur at 2.5 eV (Si) and 2.7 eV (Ge). Excellent agreement with the corresponding experimental values suggests that divalent Si and Ge defects contribute to the 5-eV absorption band and subsequent photoemissions in silicate and germanosilicate glasses. [S0163-1829(97)50724-7]

I. INTRODUCTION

The intense 5-eV photoabsorption band and subsequent photoluminescence emissions in silicate and germanosilicate glasses have been studied extensively by a large number of groups.[1–12] Recently, there has been renewed interest in identifying the origin of this 5-eV band because of its role in phase-grating formation in optical fibers.[13–15] However, the defect models responsible for this absorption band are still under debate since there is no structure-sensitive measurement for nonparamagnetic defects in glasses.

Several structural models have been proposed as likely candidates for the 5-eV absorption band. The oxygen vacancy model ($\equiv$Si-Si$\equiv$) was proposed by Arnold,[2] and correlations between the decay of the 5-eV band and the growth of E' centers under UV irradiation[4,8] have been used in support of this model. However, other workers[5,6,16] suggested that the singlet-to-singlet absorption of the oxygen vacancy occurs much higher around 7.6 eV, similar to the absorption seen in disilane.[17] An alternative model involving divalent defects ($=$Si: or $=$Ge:) was proposed by Skuja, Streletsky, and Pakovich[3] in 1984. They performed time-resolved photoluminescence measurements of oxygen-deficient glassy SiO_2, and observed two luminescence bands at 4.4 and 2.7 eV. Based on their decay time measurements, these two bands were assigned to be the luminescence emission from singlet and triplet excited states. Similar photoabsorption and photoluminescence spectra were also observed in Ge- and Sn-doped SiO_2 glasses,[7] and they were attributed to isoelectronic series of divalent Si, Ge, and Sn defects. A third model involving an oxygen deficiency center of the divacancy type associated with Ge was recently proposed by Tsai *et al.*[12] to explain the 5.16-eV absorption band in germanosilicate glasses.

Experimentally, Hosono *et al.*[8] determined that there are two components of the 5-eV band in germanosilicate glasses. One of them is bleached upon 5-eV laser illumination, and the other does not bleach but emits luminescence bands at 3.1 and 4.3 eV. The 5-eV band with luminescence was assigned to divalent Ge defects, and the 5-eV bleachable band was assigned to neutral oxygen vacancy coordinated by two Ge atoms. Theoretically, electronic excitations and photoluminescence of divalent defects and neutral oxygen vacancy in germanosilicate glasses have been studied by the semiempirical modified neglect of differential overlap (MNDO) method with cluster models.[18–21] These calculations appear to favor neutral oxygen vacancy rather than divalent defects as the origin of the 5-eV absorption band and the two photoluminescence bands.

In this paper, we performed *ab initio* quantum-chemical calculations of the electronic excitation and photoluminescence properties for divalent defects in germanosilicate glasses. The recent development of accurate excited-state techniques allows us to examine critically the validity of the divalent defect model in explaining the experimental 5-eV photoabsorption and subsequent photoluminescence emission bands.

II. THEORETICAL METHODS

We used the cluster approach, where model compounds are designed to include the important aspects of the local defect environments. Since the defect states considered in this work are quite localized, a relatively small cluster can be used to model the local region of interest. In our finite cluster model, the broken back bonds are terminated with hydrogen

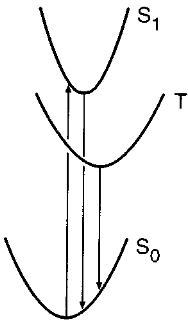

FIG. 1. A schematic of the excitation and emission energies considered in this paper.

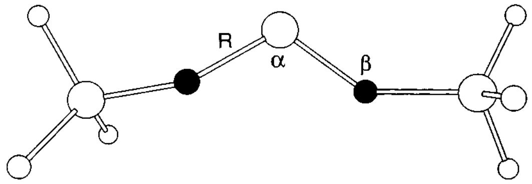

FIG. 2. A schematic of the cluster model used in this paper. Dark circles denote O, small open circles denote H, and large open circles denote Si or Ge.

to avoid artifacts from surface effects.

A schematic of the energies under evaluation is shown in Fig. 1. Initially, the geometry of the ground-state defect structure (S_0) was determined by complete optimization at the Hartree-Fock (HF) level of theory[22] with the polarized 6-31G* basis set[22] on Si, O, and H, and a contracted $6s$, $4p$, $2d$ basis set on Ge (Ref. 23) using analytical gradient techniques. For convenience, we refer to this basis as 6-31G* for the remainder of this paper. Using this geometry, the low-lying singlet electronic excitation energies ($S_0 \rightarrow S_1$) were evaluated with three different excited-state techniques. In increasing order of accuracy, these are CIS (Ref. 24) (configuration interaction with singlet excitation); CIS (D) (Ref. 25) a second-order perturbative correction applied to the CIS method; and excited-state CCSD (coupled-cluster method including single and double excitations).[26] In particular, the excited-state CCSD method is known to give accurate values (within 0.2 eV) for the low-lying electronic states of molecules. The CIS method, though less accurate, is useful to test the convergence of the calculated values with increasing basis set size as well as cluster size. The CIS (D) excitations are expected to be of intermediate accuracy. The energy of the triplet excited state (T_1) which can be well represented by a single configuration was determined by a different procedure. Separate CCSD(T) calculations[27] (including corrections for triple excitations) were performed on the ground state and the excited triplet state, and the energy difference yields the triplet excitation energy ($S_0 \rightarrow T_1$). We find (*vide infra*) that the correction for triple excitations is very small ($<$0.05 eV), providing justification for their neglect for excited singlet states. A larger basis set containing a set of diffuse s and p functions on Ge and Si and each O was used for all the excitation energy calculations.[22,23] We refer to this basis set as 6-31+G*, where + denotes diffuse functions as per standard notation.

In order to obtain photoluminescence energies, additional geometry relaxations were carried out for the excited states. The geometry of the excited singlet (S_1) and triplet (T_1) states were optimized with the CIS and HF methods, respectively, using the same basis set used for optimizing the ground state. The excitation energies evaluated at these excited-state geometries were used to derive the singlet and triplet photoluminescence energies ($S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$).

TABLE I. Structural parameters of ground-state singlet (S_0), optimized first-excited state (S_1) and triplet (T_1) (see Fig. 1 for the notations).

System	α(°)	β(°)	R (Å)
Si(S_0)	101	147	1.64
Si(S_1)	115	136	1.65
Si(T_1)	117	145	1.64
Ge(S_0)	97	143	1.77
Ge(S_1)	112	130	1.78
Ge(T_1)	114	138	1.76
α-quartz (Ref. 28)	108–111	144	1.608,1.611

III. RESULTS AND DISCUSSIONS

For divalent defects, the low-lying electronic states correspond to excitation of an electron from the lone pair on Si or Ge to the vacant π-like orbital on the same atom, leading to triplet and singlet states. The excitation energy associated with this defect (roughly 5 eV) is considerably lower in energy than those resulting from the electronic states associated with defect-free silica or molecules such as silane or germane ($>$8 eV).[17] The excitation is very localized, and is strongly perturbed only by the nearest two oxygens directly attached to the divalent Si or Ge. Atoms attached farther away appear to have very little effect on the calculated low-lying excitation energies for this defect. Since the excitation is very localized, we report results with a cluster model H_3Si-O-Si-O-SiH_3 or H_3Si-O-Ge-O-SiH_3 to represent such divalent Si or Ge defects. The central Si or Ge atom is the principal site at which the excitation occurs. A schematic of the cluster model used in this paper is shown in Fig. 2. For the cluster model, we perform complete geometry optimizations for the ground state as well as the excited singlet and triplet states. The optimized geometries have either C_2 or C_s symmetries though the excitation energies have only a weak dependence on the symmetry.

Some of the interesting geometrical parameters near the central Si or Ge are listed in Table I. First, the central O-Si-O angle of 101° for the fully optimized geometry of divalent Si is about 10° smaller than that in the α-quartz structure.[28] The O-Ge-O angle of 97° is even smaller. This is a well-known effect seen in divalent systems such as SiH_2 or GeH_2, which have even smaller bond angles due to the presence of greater p contribution to the bonding. The Si-O bond distances at the divalent center (1.64 Å) are correspondingly slightly larger than that in α quartz. The mean Si-O-Si angle of 147° is close to the value of 144° in α quartz.

TABLE II. Singlet-to-singlet excitation energies of divalent defects (eV).

System	6-31G*			6-31+G*			Expt.
	CIS	CIS(D)	CCSD	CIS	CIS(D)	CCSD	
Si	5.64	5.40	5.38	5.52	5.24	5.24	5.0 (Ref. 7)
Ge	5.56	5.14	5.13	5.48	5.05	5.05	5.1 (Ref. 8)

TABLE III. Singlet-to-triplet excitation energies of divalent defects (eV).

System	CCSD/6-31+G*	CCSD(T)/6-31+G*	Expt.
Si	3.06	3.10	3.15 (Ref. 10)
Ge	3.31	3.35	3.7 (Ref. 7)

As is well known from simple divalent systems such as SiH_2 or GeH_2, the bond angle increases on going from the ground state to the excited singlet or triplet state. Thus the central O-Si-O bond angle increases by about 15° on going from the ground state to the excited singlet or triplet state for both divalent Si and Ge. The excitation energies depend strongly on this angle. The optimized Si-O-Si angles for the excited states are somewhat smaller than the ground state.

The calculated singlet excitation energies ($S_0 \rightarrow S_1$) of divalent Si and Ge are listed in Table II. In this table, we list excitation energies using two different basis sets 6-31G* and 6-31+G*, i.e., without and with diffuse functions. We also list excitation energies calculated with the three different methods, CIS, CIS(D), and CCSD. As we can see, the excitation energies are quite convergent for different basis sets and different level of calculations. Even the simple CIS technique performs reasonably well for this system. On going from the CIS to the accurate CCSD calculation, the excitation energies decrease by 0.3–0.5 eV. The second-order perturbative CIS(D) method performs excellently, yielding results essentially identical to the more expensive CCSD method. Similar comparisons should be done in the future for other systems where correlation effects are more important. The effects of basis sets are even smaller with a maximum change of 0.2 eV from 6-31G* to 6-31+G*. Part of the reason for the rapid convergence of the calculated excitation energies is that the excitations are well localized and have valence character. Rydberg-type excitations involved in more saturated systems typically converge much slower. In general, the excitation energy for divalent Ge is slightly lower than that for Si. The calculated excitation energies of 5.2 and 5.1 eV for divalent Si and Ge are in very good agreement with the 5-eV absorptions seen for these systems.

However, the local atomic geometries in real glasses are constrained by glass networks which are not included in our cluster models. In order to test the dependence of excitation energies on the local geometries, we evaluated the excitation energies by changing the local O-Si-O and Si-O-Si angles. *The calculated excitation energies have a strong dependence on the* O-Si-O *angle at the divalent Si*. This is not surprising since the excitation is principally a localized transition at the central silicon from a lone-pair orbital (about 80% $3s$) to the vacant π-like orbital. Since this O-Si-O angle changes by 15° on going to the excited state, there is a significant difference between the excitation energies and the corresponding luminescence energies (*vide infra*). The outer Si-O-Si angles, on the other hand, perturb the calculated excitation energies only slightly. This indicates that the excitation energy is quite insensitive to small distortions in the perimeter geometries, and our cluster model can simulate the divalent defects very well.

The singlet-to-triplet absorption energies of divalent defects are listed in Table III. As mentioned above, these energies were evaluated by directly performing CCSD(T) calculations with the larger 6-31+G* basis set on the ground state and the excited triplet state. We list both the CCSD and CCSD(T) results in Table II. The CCSD(T) scheme has been well recognized to be one of the most accurate quantum-chemical schemes.[29] In all cases, the difference between the CCSD and CCSD(T) values is only 0.05 eV or less, suggesting that three-electron correlations contribute very little to the excitation energies. The calculated triplet excitation energies for divalent Si and Ge are 3.10 and 3.35 eV. For divalent Si, recently Skuja[10] performed a careful study of the direct singlet-to-triplet optical-absorption transition and derives a value of 3.15 eV, in excellent agreement with the calculations. For divalent Ge, the observed weak absorption band of 3.7 eV is in moderately good agreement with theory. More importantly, the higher triplet excitation energy for divalent Ge relative to Si is clearly reproduced by the theoretical calculations.

The energy difference between the singlet and triplet is a rough measure of twice the exchange energy. As pointed out previously by Skuja,[7] the singlet-triplet splitting for Si is about 0.4 eV larger than that for Ge, indicating the more diffuse nature of the orbitals for the latter.

The geometry of the excited singlet state was optimized at the CIS/6-31G* level. Force-constant evaluations were performed to ensure that the excited-state geometry was fully relaxed. Additional calculations were then performed at the CIS*(D)* and CCSD levels with the 6-31+G* basis set to obtain photoluminescence energies which are listed in Table IV. The available experimental values are also listed for comparison. As in the case of excitation, the calculated $S_1 \rightarrow S_0$ photoluminescence energies for divalent Si (4.49 eV) and Ge (4.13 eV) are both in excellent agreement with the corresponding experimental values of 4.4 and 4.3 eV, respectively. The difference between the CIS and CCSD values are again similar, 0.3–0.5 eV. The perturbative CIS(D) scheme again yields results very close to the CCSD method.

To study the triplet-to-singlet luminescence, we fully op-

TABLE IV. Singlet-to-singlet photoluminescence of divalent defects (eV).

System	CIS/6-31+G*	CIS(D)/6-31+G*	CCSD/6-31+G*	Expt.
Si	4.82	4.46	4.49	4.4 (Ref. 7)
Ge	4.61	4.06	4.13	4.3 (Refs. 7 and 8)

TABLE V. Triplet-to-singlet photoluminescence of divalent defects (eV).

System	CCSD/6-31+G*	CCSD(T)/6-31+G*	Expt.
Si	2.48	2.53	2.7 (Ref. 10)
Ge	2.65	2.70	3.1 (Ref. 7)

timized the triplet state of our cluster model with the HF/6-31G* model. As mentioned earlier, the central O-Si-O angle for the excited triplet state is very similar to that in the excited singlet state, and is about 15° larger than that in the ground state. The vertical luminescence emission $(T_1 \rightarrow S_0)$ is obtained from the energy difference of singlet and triplet CCSD(T) calculations for this geometry. Our calculated results and experimental values are listed in Table V. The CCSD and CCSD(T) results are all again within 0.05 eV of each other. The $T_1 \rightarrow S_0$ energy of divalent Si obtained in our calculation is 2.53 eV which is in good agreement with the 2.7-eV emission band observed in optical measurements.[7] Again, as in the case of absorption, the value for Ge (2.7 eV) is larger than that of Si, and is in moderately good agreement with the experimental value of 3.1 eV. If the constraints present in the real glass do not allow complete relaxation in the excited state, the observed photoluminescence values will be somewhat greater than those calculated assuming complete relaxation.

Sokolov and Sulimov[19] recently performed semiempirical MNDO calculations on divalent Si and Ge defects. They obtained reasonable agreement with experiment for Si, while the corresponding values for Ge were significantly lower than the experimental values (by 1–2 eV). Based on this discrepancy, they ruled out the divalent model for oxygen deficient defects in glasses. However, our *ab initio* results are in considerably better agreement with experiment in all cases, suggesting a reexamination of the applicability of MNDO in the case of excitations involving germanosilicate glasses.

IV. CONCLUSIONS

In this paper, we performed a thorough investigation of the singlet-to-singlet as well as singlet-to-triplet photoabsorption and photoluminescence calculations for the divalent defect models for Si and Ge in germanosilicate glass. The overall mean agreement between the theoretical and experimental values for eight different energetic quantities is within 0.2 eV. Thus we can clearly conclude that divalent Si or Ge is an excellent model for the 5.0-eV absorption band and the subsequent photoluminescence emission bands. We are currently performing a similar investigation of the excited states associated with the neutral oxygen vacancy, to understand the nature of its optical absorptions fully.

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