Photoabsorption of the neutral oxygen vacancy in silicate and germanosilicate glasses: First-principles calculations

Boris B. Stefanov and Krishnan Raghavachari

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

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The photoabsorption of the neutral oxygen vacancy defects in silicate and germanosilicate glasses has been studied by first-principles quantum chemical techniques. The lowest singlet-to-singlet excitations in these defects occur around 7.0 eV, and involve promotion of an electron from a bonding orbital between the adjacent Si (or Ge) atoms to a diffuse Rydberg-type orbital. Such excitations are too high in energy to contribute significantly to the 5 eV absorption band in silicate and germanosilicate glasses. [S0163-1829(97)00234-8]

INTRODUCTION

The prominent 5 eV photoabsorption band in silicate and germanosilicate glasses has been the focus of a large number of experimental and theoretical investigations.[1–17] Several structural models have been proposed as likely explanations for the origin of this band, and although there have been no definitive assignments, it has generally been accepted that a neutral oxygen vacancy and a divalent defect are the two most likely candidates.

The oxygen vacancy model ($\equiv X - Y \equiv$; $X, Y =$ Si,Ge) 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. The recent semiempirical modified neglect of differential overlap (MNDO) calculations of Sulimov and co-workers[16,17] have provided support to this model. However, other workers[5,6,13] have suggested that the singlet-to-singlet absorption of the oxygen vacancy occurs much higher, around 7.6 eV, similarly to the absorption seen in disilane.[18]

An alternative model involving divalent defects ($=$Si: or $=$Ge:) was proposed by Skuja, Streletsky, and Pakovich.[3] 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 attributed to luminescence emissions from singlet and triplet excited states of divalent defects.[7]

We recently performed an accurate theoretical investigation of divalent Si and Ge defects using cluster models.[19,20] The calculated excitation energies as well as luminescence band energies are in excellent agreement with the experimental results of Skuja and co-workers[3,7] and offer a strong support for the divalent defect model. In this paper, we report an analogous detailed *ab initio* study of the electronic excitation energies for the neutral oxygen vacancy defects in silicate and germanosilicate glasses. The recent development of accurate excited-state techniques allows us to critically examine the plausibility of this defect model in explaining the experimental 5 eV photoabsorption bands.

THEORETICAL METHODS

As in our previous studies,[19,20] we have 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. The broken back bonds in our finite cluster model are terminated with hydrogen atoms to avoid artifacts from surface effects.

In the present work, geometry determinations are performed using Hartree-Fock theory with a polarized $6\text{-}31G^*$ basis set.[21] The basis set is known to yield reliable molecular geometries for a wide variety of systems.[21] Using this geometry, the low-lying singlet electronic excitation energies were evaluated with three different excited-state techniques. In increasing order of accuracy, these are the configuration interaction with single substitutions[22] (CIS), a second-order perturbative correction applied to the CIS method[23] [CIS(D)], and the excited-state coupled-cluster method including single and double substitutions[24] (CCSD). 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.[25] In order to describe both valence and Rydberg-type excitations on an equal footing, we have used larger basis sets containing diffuse s and p functions in these calculations. Initially we performed calculations with the CIS and CIS(D) methods using a $6\text{-}31G^*$ basis set augmented with two sets of diffuse s and p functions on each Si or Ge. Later we found that a basis set containing two sets of diffuse s and p functions with average exponents centered at the bond midpoint yields essentially identical excitation energies (average deviation between the two basis sets is only 0.02 eV). Here we report results with this basis set[26] which we denote as $6\text{-}31G^*[2+]$. All the calculations have been performed with modified versions of the GAUSSIAN-94[27] and TITAN[28] electronic structure packages.

RESULTS AND DISCUSSION

When there is an oxygen vacancy, the neighboring Si or Ge atoms can come together and form a chemical bond. We have investigated oxygen vacancies with different possible neighboring atoms and represent them using the common notation,[16,17] viz. V(SiSi), V(SiGe), and V(GeGe), showing the atoms adjacent to the vacant site. Since our models describe localized electronic excitations involving the defect region, we expect that the excitation energies are determined

TABLE I. Geometric parameters [(Å) and (°)] of the $(HO)_3 X$-$Y(OH)_3$ molecules used in this study (optimized at HF/6-31G^* level of theory).

X/Y	Symmetry	X-Y	X-O	Y-O	X-Y-O	Y-X-O	X-O-H	Y-O-H
Si/Si	S_6	2.32	1.65	1.65	110.7	110.7	116.7	116.7
Si/Si	C_2	2.32	1.64	1.64	103.1	103.1	116.5	116.5
			1.64	1.64	110.5	110.5	116.9	116.9
			1.64	1.64	117.4	117.4	118.0	118.0
Si/Ge	C_3	2.37	1.63	1.77	112.9	109.4	118.4	113.2
Si/Ge	C_1	2.37	1.63	1.76	100.3	104.2	116.7	113.4
			1.63	1.76	118.4	105.1	117.3	115.2
			1.63	1.77	118.8	117.6	118.7	115.9
Ge/Ge	S_6	2.39	1.76	1.76	111.8	111.8	113.8	113.8
Ge/Ge	C_2	2.40	1.76	1.76	106.7	106.7	113.6	113.6
			1.76	1.76	113.9	113.9	115.0	115.0
			1.76	1.76	114.2	114.2	116.1	116.1

primarily by the two defect Si (or Ge) atoms and their attached oxygen atoms. Thus we start with the clusters $(HO)_3$-Si-Si$(OH)_3$, $(HO)_3$Si-Ge$(OH)_3$, $(HO)_3$Ge-Ge$(OH)_3$ to represent the oxygen vacancy in the case of V(SiSi), V(SiGe), and V(GeGe), respectively. In order to see if the size of our chosen cluster is reasonable, in the case of V(SiSi), we also consider a larger cluster model $(H_3SiO)_3$Si-Si$(OSiH_3)_3$, similar to the cluster used previously in the semiempirical MNDO studies of Sulimov and co-workers.[16,17]

For each of the cluster models, we have considered several possible geometrical arrangements (conformations). We first report results for a structure containing a threefold symmetry axis along the X-Y bond (X,Y=Si or Ge). Such a structure has S_6 symmetry for V(SiSi) and V(GeGe), and C_3 symmetry for V(SiGe). Within this symmetry, all the geometrical parameters have been completely optimized at the HF/6-31G^* level of theory (Table I). The optimized Si-Si distance in V(SiSi) is 2.32 Å, very similar to the values obtained by Sulimov and Sokolov with MNDO.[16] The angle Si-Si-O is close to the tetrahedral angle. As expected, the Si-Ge and Ge-Ge distances in the analogous Vi(SiGe) and V(GeGe) defects (2.37 and 2.39 Å, respectively) are slightly longer. In this paper we also analyze the dependence of the computed energies on the value of this distance.

The excitation energies evaluated for each of these defects with the CIS and CIS(D) techniques are listed in Table II. In addition, for V(SiSi), we list the results evaluated with the CCSD method which helps to assess the reliability of the CIS and CIS(D) techniques. These calculations were carried out with two different basis sets, namely 6-31G^* and 6-31G^*[2+](without and with diffuse functions, respectively).

There are two immediate striking observations to be made on the basis of this data. First, the 6-31G^* basis set is totally inadequate, yielding excitation energies that are too large by up to 2 eV. The large change on going to the 6-31G^*[2+] basis set is indicative of an excitation into a diffuse orbital (*vide infra*). Second, the CIS method is also inadequate in describing the excitation energies for this system. For example, for V(SiSi), the CIS method with the 6-31G^*[2+] basis set yields a lowest singlet-to-singlet excitation energy of 8.36 eV, a substantial overestimate compared to the more accurate treatments. Electron-correlation effects, included in the CIS(D) and CCSD methods, stabilize the excited state significantly and lower the excitation energy. The CIS(D) method yields an excitation energy of 6.74 eV, close to the CCSD value of 6.97 eV. From a consideration of other similar structures, it appears that for the oxygen vacancy defects, the CIS(D) method yields excitation energies with a mean deviation of $\approx$0.2 eV from the accurate CCSD values.

The nature of the electronic excitations is illuminating. The lowest excitation is not a simple bonding-antibonding

TABLE II. Excitation energies (eV) for the lowest three singlet excited states of the $(HO)_3 X$-$Y(OH)_3$ molecules (S_6/C_3 isomers).

X/Y (symmetry)	Excited state	6-31G^*			6-31G^*[2+]		
		CIS	CIS(D)	CCSD	CIS	CIS(D)	CCSD
Si/Si	s	10.35	9.06	9.08	8.36	6.74	6.97
(S_6)	p_z	10.14	8.80	8.84	8.62	6.97	7.21
	$p_{x,y}$	8.88	7.92	7.93	8.55	7.29	7.39
Si/Ge	s	10.06	8.63		8.45	6.71	
(C_3)	p_z	9.68	8.31		8.67	6.99	
	$p_{x,y}$	8.69	7.59		8.42	7.12	
Ge/Ge	s	9.85	8.39		8.67	6.85	
(S_6)	p_z	9.40	8.06		8.64	6.94	
	$p_{x,y}$	8.59	7.37		8.37	7.00	

transition involving the Si-Si bond, as obtained by Sulimov and Sokolov.[16] While it is dominantly a one-electron transition, it is best described as a promotion of an electron from the Si-Si bonding orbital to a diffuse orbital (Rydberg-type excitation). The inclusion of diffuse functions in the basis set is clearly of importance to describe such excitations. This is reminiscent of the lowest electronic excitation in the Si_2H_6 molecule[18] which is from a Si-Si bonding orbital to a $4s$-type Rydberg orbital. The CCSD method yields an excitation energy of 7.6 eV for Si_2H_6, in excellent agreement with the experiments.[18] In addition, the singlet-to-singlet excitation energies for the V(SiGe) and V(GeGe) defects have been obtained with the CIS(D) method. The resulting values (Table II) are quite similar to those for V(SiSi).

Analysis of other low-lying excitations also reveals similar Rydberg-type character. The second and third excitations have p-type character along the bond and perpendicular to the bond, respectively (Table II). Such excitations occur about 0.1–0.5 eV higher in the different systems and have much larger absorption cross sections due to the favorable dipole selection rules.

We have also considered other possible conformational arrangements for the defect geometries. The excitation energies depend only weakly on such structural variations. The most stable conformation for V(SiSi) has C_2 symmetry. It is about 0.1 eV more stable than the S_6 structure considered earlier. This is mainly due to the presence of internal hydrogen bonding between different −OH groups in the C_2 isomer. The Si-Si-O angles vary between 103 and 117° (Table I) due to this hydrogen bonding. Though such a structure is probably unrealistic to describe the oxygen vacancy, we find that the excitation energy is not strongly dependent on such details. The energy depends principally on the Si-Si distance, which in the C_2 structure is, in essence, identical to the corresponding distance in the S_6 isomer (2.32 Å). Consequently, the lowest excitation energy in the isomer at the CCSD level, 7.21 eV, is quite close to the value of 6.97 eV seen earlier for the S_6 isomer.

Similar structures were also considered for V(SiGe) and V(GeGe). They are even less sensitive to the structural details. The analogous C_2 isomer for V(GeGe) and the C_1 isomer for V(SiGe) have very similar excitation energies.

In order to test the adequacy of our defect model cluster size, we have performed CIS(D) calculations for V(SiSi) using a larger cluster $(H_3SiO)_3Si$-$Si(OSiH_3)_3$ (Fig. 1). There is very little change in the excitation energy upon going to the larger cluster, consistent with the localized nature of the electronic excitations. The CIS and CIS(D) excitation energies for the large cluster, 8.6 and 7.0 eV, respectively, are very close to the values of 8.4 and 6.7 eV seen for the S_6 isomer for the small cluster. The optimized Si-Si distance in the larger cluster (2.32 Å) as well as the Si-Si-O angles are also very similar to those in the smaller cluster.

Our calculations have clear implications. First, for the structures considered so far with relaxed geometries, the calculated lowest singlet-to-singlet excitation energies cluster around 7.0 eV. Their values are substantially larger than 5 eV and thus excitations involving the relaxed oxygen vacancy do not explain the 5 eV excitation band in glasses. We showed recently that divalent Si or Ge defects, on the other hand, have excitations very close to 5 eV.[19,20]
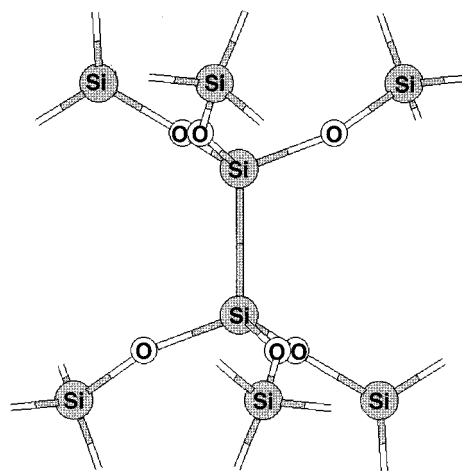

FIG. 1. The $(H_3SiO)_3Si$-$Si(OSiH_3)_3$ cluster used in this work (the terminating H atoms are not shown).

Our conclusions are completely opposite to those reached by Sulimov and co-workers[16,17] using the semiempirical MNDO technique. Using relaxed cluster geometries for the oxygen vacancy, they obtain singlet-to-singlet excitation energies ranging from 4.8 to 5.3 eV for a variety of models. Our CCSD values, which should be very accurate, are considerably higher. The discrepancy is not due to the size of the cluster since for V(SiSi) the same sized cluster was used in both studies. In addition, the relaxed Si-Si distance is very similar in both studies. Another major difference between the two studies is the qualitative nature of the lowest excited state. Contrary to the bonding-antibonding character of the transition, predicted by MNDO, we obtain a transition from a bonding orbital to a diffuse orbital. Since MNDO does not contain any diffuse functions, such excited states cannot be treated adequately with this technique. We conclude that MNDO *is not adequate for obtaining accurate excitation energies in such systems.*

While we can definitively rule out the relaxed oxygen vacancy model, other related models involving partially relaxed or unrelaxed such vacancies, have been proposed to explain the 5 eV photoabsorption. The underlying argument in these models is that in the vitreous environment of the germanosilicate glass, it is possible for Si-Si distances to deviate from the optimal value of 2.3 Å. In order to consider such a possibility, we have performed additional calculations with stretched bond lengths on the S_6 structure. In these

TABLE III. Dependence of lowest three singlet excitation energies (eV) of $(HO)_3Si$-$Si(OH)_3$ on the Si-Si bond length (CCSD/6-$31G^*[2+]$ level for the S_6 isomer).

Δ(Si-Si) (Å)	Excited-state type		
	s	p_z	p_{xy}
0.0	6.97	7.21	7.39
0.1	6.84	7.05	7.25
0.2	6.71	6.88	7.10
0.3	6.57	6.71	6.95
0.4	6.43	6.53	6.79
0.5	6.30	6.35	6.64

calculations, the Si-Si distance was fixed at distances ranging from 2.32 to 2.82 in steps of 0.1 Å. Electronic excited states at these geometries were then evaluated with the $6\text{-}31G^*[2+]$ basis set and are listed in Table III. For a bond stretching of 0.2 Å, the excitation energy decreases by 0.2–0.3 eV. We anticipate our CCSD model to be sufficiently reliable for such bond length changes. On stretching the bond by 0.5 Å, the excitation energies decrease by as much as 0.7–0.8 eV, though theoretical calculations for such far-from-equilibrium bond distances are expected to have larger uncertainties.

The calculations reported above indicate that the excitation energy does decrease at stretched bond lengths. However, a completely unrelaxed geometry with a Si-Si distance of 3.1 Å is not a stable arrangement and is unlikely for the ground state. Partially relaxed geometries with a distribution of distances are likely to yield only a broad shoulder of the 7 eV excitation.

Other authors have suggested that the 5 eV band results from a singlet-to-triplet excitation of the oxygen vacancy.[5,6] However, singlet-to-triplet transitions are unlikely to yield strong absorptions, particularly for Si. We are currently evaluating the excitation energies for the low-lying triplet states to see if such a model is relevant.

ACKNOWLEDGMENTS

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