Concerning the Interaction of Atomic Silver with a Silicon Monoxide Ligand

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Ab initio quantum mechanical studies of the Ag + SiO complex using double zeta (DZ) and double zeta plus polarization (DZP) function basis sets, including configuration interaction, show that the silver atom is O-bonded in a quasi-linear orientation, not Si-bonded and bent as previously concluded from experimental studies.

The chemistry of transition metal complexes containing carbonyl (CO) ligands is extensive and well understood.[1] The analogous silicon monoxide (SiO) chemistry is far less well understood but is important because of the resemblance of silicon to carbon[2] and its relevance to silicon wafer technology.[3] Recently, experimental work on the matrix isolated interactions of Ag and SiO has been reported[3] and a strongly bent structure for the resulting complex proposed.

We here describe the results of an *ab initio* theoretical study of this novel complex with double zeta (DZ) and double zeta plus polarization (DZP) function basis sets including the effects of electron correlation at the singly and doubly excited configuration interaction (CISD)[4] level of theory.

The silver atom DZ basis set was based upon the 15s9p8d primitive Gaussian set of Veillard and Dedieu[5] to which was added two p-functions (orbital exponents α_p = 0.253 and 0.0902). The resulting 15s11p8d set was contracted‡ to 8s6p4d. The silicon and oxygen basis sets used were the standard Huzinaga–Dunning[6] contractions. A larger DZP quality basis set for silver was formed by adding an s-function (α_s = 0.015) and a d-function (α_d = 0.09) to the DZ basis set described above. For silicon and oxygen, DZP basis sets were formed by adding d-functions of exponent 0.5 and 0.85 respectively to the above DZ basis sets.

In order to determine the geometric structure of the Ag + SiO complex unambiguously, three geometry optimizations were performed starting from the experimental geometry,[3] namely the bond lengths Ag–Si = 2.5 and Si–O = 1.5 Å and the bond angle Ag–Si–O = 90°. Structural optimizations were carried out with the DZ basis at the SCF and CISD levels of theory§ and with the DZP basis at the SCF level only, using SCF[7] and CISD[8] analytic gradients. In each case a linear (Ag–O–Si) structure resulted. In addition, the geometry of linear Ag–O–Si at the DZP/CISD level of theory was also determined. At the DZP/CISD level of theory the linear Ag–O–Si isomer is 6.9 kcal mol^{-1} (1 cal = 4.184 J) below the suggested experimental geometry given above. The geometric parameters of linear AgOSi at the DZ/SCF, DZ/CISD, DZP/SCF and DZP/CISD levels of theory are given in Table 1 along with vibrational frequencies, determined *via* finite difference methods for CISD[8] and analytically for SCF wavefunctions.[9]

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‡ The 15s11p8d primitive set was contracted to 7 2 111111 in the s space; 5 2 11 11 in the p and 5 111 in the d space. Contraction coefficients were obtained from an atomic SCF calculation on the ^2S state of Ag with the uncontracted basis set. After adding the two p-functions, the silver atom SCF energy with the 8s6p4d basis set was −5194.21066 Hartrees.

§ In the CISD expansion the following atomic orbitals were frozen: Ag(1s,2s,2p,3s,3p,4s,3d,4p), O(1s) and Si(1s,2s,2p).

Table 1 Geometric parameters (in Å), binding energies[a] (in kcal mol^{-1}), harmonic vibrational frequencies[b] (in cm^{-1}), and SiO isotopic frequency shifts (in cm^{-1}) for AgOSi ($^2\Sigma^+$). Note that while the DZP CISD vibrational analysis refers to the linear structure, the actual DZP CISD equilibrium geometry lies one cm^{-1} lower in energy, with θ_e(Ag–O–Si) = 169°.

	DZ		DZP		EXPT[c]
	SCF	CISD	SCF	CISD	
Ag–O distance	2.427	2.411	2.587	2.511	
O–Si distance	1.548	1.577	1.488	1.510	
Binding energy	6.5	6.8	3.7	5.0	
ω_1	1241	1154	1391	1308	1163
ω_2	132	132	91	107	
ω_3	48	27	28	$3i$	
$\Delta\omega_1(^{28}\text{Si}-^{29}\text{Si})$	7.7	7.1	8.7	8.1	7.1
$\Delta\omega_1(^{28}\text{Si}-^{30}\text{Si})$	14.9	13.7	16.9	15.8	14.0
$\Delta\omega_1(^{16}\text{O}-^{18}\text{O})$	45.3	42.3	50.2	47.5	41.7

[a] All binding energies calculated relative to Ag + SiO separated by 500 a.u. with the Si–O bond length optimized in the super-molecule. [b] All frequencies (and frequency shifts) calculated with the ^{107}Ag isotopic mass. [c] EXPT = experiment.

Unlike the DZ/SCF, DZ/CISD, and DZP/SCF structures, the DZP/CISD geometry is not a local minimum on the potential energy surface. Instead it has a very small 2.3 cm^{-1} imaginary bending frequency leading to C_s symmetry structures. Thus, a reoptimization of the Ag–O–Si angle was performed with DZP/CISD energy points in C_s symmetry. This resulted in a bond angle of 169°. Re-optimizing the Ag–O bond length at this angle gave no change in the bond length. The resulting structure lies only one wavenumber below the optimized linear geometry. Therefore in each of the four cases the Ag + SiO complex is unambiguously O-bonded and either linear or quasi-linear.¶

Turning now to the predicted vibrational frequencies (Table 1), the DZ/CISD results can be seen to be fortuitously good, being only 9 cm^{-1} in error relative to experiment, an effect noted by other authors for smaller molecules.[10] The isotopic frequency shifts of the Ag + SiO complex observed experimentally are reproduced well by both DZ and DZP/CISD methods. Interestingly, the ^{28}Si–^{29}Si, ^{28}Si–^{30}Si, and ^{16}O–^{18}O isotopic frequency shifts in the complex differ only minimally from those of free SiO.[11,12] Indeed, these data coupled to the observed 63 cm^{-1} shift of the vibrational frequency of free SiO to SiO in the complex together suggest a weakly perturbed SiO unit.

That the ligand linkage is Ag–OSi rather than Ag–SiO should not be totally surprising. The same reversal has been observed in experimental[2,13] and theoretical[14] work on proton and hydrogen atom addition to SiO/CO and SiS/CS systems. The H (or H$^+$) in these more strongly bound systems shows unequivocal preference for the C end of CO and CS and the X end of SiX species. This parallel with the weakly bound AgOSi complex may be rationalized by the similar electron configuration in the atom (*i.e.* s^1 valence configuration).

In conclusion we have found that the complex of Ag + SiO is a weakly bound linear or quasi-linear Ag–O–Si molecule. Isotopic shifts and harmonic vibrational frequencies determined theoretically agree with those observed experimentally. An Si-bonded triangular isomer proposed earlier[3] has not been found. The reason the vibrational frequency modelling suggested a triangular Ag–Si–O molecule[3] instead of the quasi-linear Ag–O–Si species found here may be traced to the assumptions made in the valence force field calculations for the Ag–O–Si linked structures. Particularly, the assumption of the bond length Ag–O = 2.00 Å and $\nu_{\text{Ag–O}}$ = 400 cm^{-1} is more indicative of a covalently bonded complex, and lead to significantly different isotopic vibrational frequency shifts than those observed experimentally or found here in our *ab initio* theoretical studies for which the bond length Ag–O ~ 2.5—2.6 Å.

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¶ Since the change in Ag–O bond length in moving from the DZ to the DZP basis is quite large (at both levels of theory) the effects of larger basis sets at the SCF level of theory were carefully examined. Addition of a third set of p-functions (α_p = 0.03) and a set of ten Cartesian f-functions (α_f = 0.12) to the silver DZP basis set increased the Ag–O distance by only 0.007 to 2.594 Å and left the Si–O distance unchanged. The Si–O harmonic vibrational frequency changed by only 1 cm^{-1}, and the isotopic shifts were unchanged. A second study adding a third p-function as above and a second set of d-functions with α_d = 0.03 to yield an effective triple-zeta plus double polarization basis set for silver, in conjunction with Dunning's triple-zeta contraction of Huzinaga's 9s5p set for oxygen with α_d(O) = 1.5, 0.35, and McLean and Chandler's 6s5p contraction of Huzinaga's 12s9p silicon basis set with α_d(Si) = 1.0, 0.25, yielded bond lengths Ag–O = 2.608 and O–Si = 1.483 Å. Here the Si–O isotopic frequency shifts differed by only 0.1—0.2 cm^{-1} from the DZP values. Finally, uncontracting the 15s9p8d primitive set to 10s6p5d in a 6 111111111, 411111, 41111 manner and adding the one s-, two p- and one d-function as for the DZP basis with the standard Si,O DZP basis set led to the bond lengths Ag–O = 2.632 Å, an increase of 0.045 Å compared to the DZP silver atom basis set. Despite the bond distance change, the absolute Si-O harmonic vibrational frequencies and isotopic shifts remain unchanged. Thus larger basis sets, at least at the SCF level of theory, do not change our results in any important way. Each SCF equilibrium geometry is linear, with Ag–O–Si linkage.

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