

## A Bridge Structure for the Ag ··· SiO Adduct†

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*Ab initio* quantum mechanical calculations using split valence plus polarization function (MIDI\*) basis sets including electron correlation correction (MP2) show that the bridge structure, where the metal atom interacts with both ends of the SiO molecule, is a stable adduct and the calculated electronic structure is in better agreement with recent ESR observations than the linear structure proposed earlier.

Monomeric Ag + SiO adduct was first characterized from the *in situ* IR spectrum of a condensed mixture of silicon, silica, and silver.<sup>1</sup> A force-field analysis of the vibrational frequencies suggests a bent (side-on) structure with the Ag bridging the Si and O atoms.<sup>1</sup> This proposal was followed immediately by a theoretical investigation by Schaefer *et al.*<sup>2</sup> The calculations failed to locate the bridge structure but instead suggested a weakly interacting linear adduct with the unpaired electron localized on the Ag atom as the most stable isomer. The calculated isotopic shifts in the Si–O stretch mode are in fair agreement with the experiment but the predicted shift in the Si–O stretching vibration from the free molecule to the complex is significantly lower than the observed value. Recently, the ESR spectrum of the mono-adduct prepared from co-condensing Ag and SiO vapour in a rotating cryostat has been measured by Mile *et al.*<sup>3</sup> An analysis of the spectrum gives a 75% s spin density on the Ag atom. This result indicates a small but still significant participation of the Ag p orbitals in the bonding. Evidently, the ESR observation is inconsistent with the predicted linear adduct structure. In view of this new experimental finding, the possible existence of a bridge (bent) structure is re-examined with *ab initio* quantum mechanical calculations.

The Huzinaga's<sup>4</sup> split valence basis sets augmented with a set of d polarization function on both Si and O atoms as well as p and d functions on Ag atom (MIDI\*) were used in the calculations. Geometry optimization with analytical gradients was performed at the Hartree–Fock (UHF and ROHF) level and then including the effects of electron correlations by the Moller–Plesset perturbation theory to the second order (MP2).<sup>5,6</sup> The nature of the stationary points was characterized through the evaluation of the harmonic vibrational frequencies. The results of the calculations are summarized in Table 1.

Three different configurations of the Ag + SiO adduct were chosen to start the geometry optimization processes. For the two end-on structures where the Ag bonded either to Si or to the O atom with the valence angle set initially to 120°, both the UHF and ROHF calculations predict no significant binding for the Si-bonded structure and the optimized linear geometry has a very long Ag···Si bond of 4.0 Å. The O-bonded structure also converged to a linear geometry ( $2\Sigma^+$ ) (Table 1). The ROHF and UHF optimized structures are almost identical. The Ag–O bond of 2.390 Å is longer than the sum of the respective covalent radius. The Si–O bond of 1.506 Å is only 0.005 Å longer than that of the free molecule computed at the same level of theory. The results obtained here are similar to those obtained previously and substantiate the finding that the Ag atom prefers to bond through the O atom and that the

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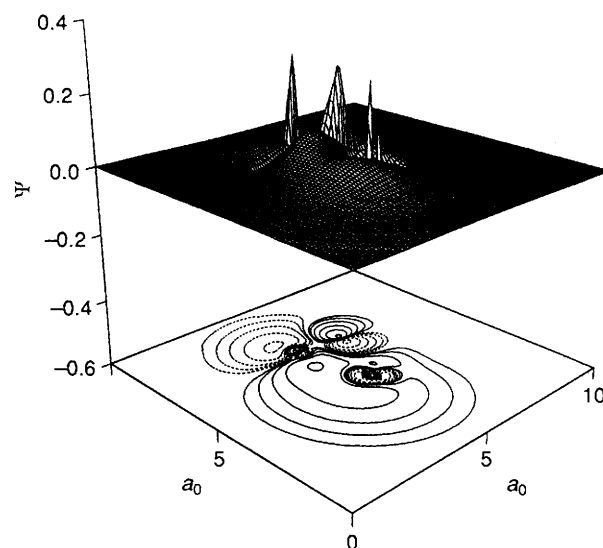
**Table 1.** Geometric parameters (Å), binding energies<sup>a,b</sup> (kcal mol<sup>-1</sup>), and harmonic vibrational frequencies (cm<sup>-1</sup>) for the linear and bridge SiOAg adducts.

	UHF	ROHF	UMP2
<b>Linear</b>			
$r(\text{Si-O})$	1.506	1.506	
$r(\text{O-Ag})$	2.390	2.391	
Binding energy	-11.7	-11.5	-12.7 <sup>c</sup>
$\omega_1$	1333	1334	
$\omega_2$	144	144	
$\omega_3$	57	56	
$\Delta\omega_1^c$	0	-1	
$\Delta\omega_1(^{28}\text{Si}-^{29}\text{Si})$	8	8	
$\Delta\omega_1(^{28}\text{Si}-^{30}\text{Si})$	16	16	
$\Delta\omega_1(^{16}\text{O}-^{18}\text{O})$	49	49	
$\langle S^2 \rangle$	0.77		
<b>Bridge</b>			
$r(\text{Si-O})$	1.541	1.526	1.590
$r(\text{O-Ag})$	2.393	2.425	2.446
$\angle(\text{Si-O-Ag})^e$	85.4	92.3	75.2
Binding energy	-10.2	-8.7	-18.0
$\omega_1$	1128	1208	1024
$\omega_2$	214	202	208
$\omega_3$	143	51	182
$\Delta\omega_1^c$	204	124	20
$\Delta\omega_1(^{28}\text{Si}-^{29}\text{Si})$	7	8	6
$\Delta\omega_1(^{28}\text{Si}-^{30}\text{Si})$	14	15	12
$\Delta\omega_1(^{16}\text{O}-^{18}\text{O})$	40	43	37
$\langle S^2 \rangle$	0.78		0.79

<sup>a</sup> Energy relative to a SiO...Ag separation of 200 Å. <sup>b</sup> 1 kcal = 4.184 kJ. <sup>c</sup> Calculated at the UHF optimized geometry. <sup>d</sup>  $\omega_1(\text{Si-O}) - \omega_1(\text{Si-O} \cdots \text{Ag})$ .

energy of interactions is very small. The calculated isotopic frequency shifts for the SiO stretch ( $\omega_1$ ) are in good agreement with experiment.<sup>1,2</sup> Based on this result alone, it would be easily concluded that the experimental structure is linear.<sup>2</sup> This assignment, however, is not entirely satisfactory. The calculations predict almost no change in the SiO stretching vibration from the free molecule to the adduct whilst a shift of 63 cm<sup>-1</sup> to lower frequency was observed in the experiment.<sup>1</sup> Furthermore, as mentioned above, the spin distribution in the linear structure is inconsistent with that derived from the ESR spectrum.<sup>3</sup> It is noteworthy that the calculated properties presented here are in complete agreement with those reported previously.<sup>2</sup>

A third geometry optimization was carried out with the Ag atom placed symmetrically above the SiO molecule at an Ag-Si distance of 3.1 Å. Interestingly, the ROHF calculation converges to a bent structure with  $\angle\text{Si-O-Ag}$  92.3°. The Ag-O distance is 2.425 Å and is longer than that of the linear isomer. The most noticeable change is a lengthening of the Si-O bond by 0.03 Å compared with that in the free molecule. The UHF geometry optimization gives a very similar result but the geometry of the complex is quite different. The Ag-O bond becomes shorter, the Si-O bond even longer, and the  $\angle\text{Si-O-Ag}$  bends towards the Si atom. These geometry changes indicate increased interactions between the Ag and Si atom and the strength of the interactions is enhanced with spin polarization. The bent structures were identified as genuine minima from their positive vibrational frequencies. Despite a lengthening of the SiO bond, the theoretical isotopic SiO stretching frequency shifts are similar to that in the linear adduct. Therefore, isotopic shifts are not good indicators for distinguishing between linear and bent structures. The most significant result, however, is the prediction of a lower SiO stretch in the bent adduct relative to that of the free molecule.



**Figure 1.** SOMO wave function ( $\Psi$ ) of the bridge AgSiO adduct at the MP2 optimized geometry. The contours used are:  $\pm(0.2, 0.1, 0.05, 0.025, 0.0125, \text{ and } 0.00625) (e^3/a_0)^{1/2}$ .

The frequency shift is 124 cm<sup>-1</sup> from ROHF and 204 cm<sup>-1</sup> from UHF calculations. In comparison with the linear structure, the O-Ag stretching frequency ( $\omega_2$ ) has increased to about 200 cm<sup>-1</sup> as a result of a stronger bond. To improve the theoretical results, the bent structure was reoptimized at the UMP2 level of theory. The inclusion of electron correlation has a dramatic effect on the Ag-Si-O angle where the Ag atom moves even closer to the Si end. The Ag atom is now straddled over the SiO molecule with  $\angle\text{Si-O-Ag}$  75.2° and the distances between the Ag and the O and Si atoms are 2.446 and 2.553 Å, respectively. The interactions between Ag and Si have obviously been greatly enhanced with a concomitant weakening in the SiO bond. Consequently, the Si-O-Ag bending frequency ( $\omega_3$ ) is increased to 182 cm<sup>-1</sup> and the SiO stretch is 20 cm<sup>-1</sup> lower than that in the free molecule.† Once again the isotopic shifts are relatively insensitive to the molecular geometry and the level of theoretical treatment.

The binding energy of the linear structure is slightly lower than that of the bent structure at the Hartree-Fock level but the order of stability is reversed when the effects of electron correlation are included. In the bent structure, the  $\pi$  system on the SiO molecule is in a better position to overlap with the Ag orbitals. The bonding can be envisaged as a donation of electrons from the metal 5s to the silicon dominated antibonding SiO  $\pi^*$  and back-donation from the oxygen dominated  $\pi$  to the empty metal 5p orbital. The Mulliken atomic charges<sup>7</sup> on the Si, O, and Ag in the bridge adduct are +0.35e, -0.65e, and +0.31e respectively. The charge distribution in the free molecule is +0.62e on Si and -0.62e on O. Therefore, the interactions between the SiO and Ag result in a net charge transfer of 0.35e from the metal. This effect is clearly reflected in the contour plot of the singly occupied molecular orbital (SOMO) wave function depicted in Figure 1. The charge donation is through the Ag 'sp' orbital into the empty  $\pi^*$  orbital of SiO which is mostly Si in character. The SOMO also shows that the unpaired spin is predominantly Ag 5s with a small p contribution. The calculated atomic spin population is 0.52, 0.32, and 0.20 on the Ag, O, and Si atom, respectively. Furthermore, the spin density on the Ag atom is composed of about 80% s and 20% p.

† The MIDI\* MP2 Si-O bond length is 1.569 Å and  $\omega(\text{Si-O})$  is 1044 cm<sup>-1</sup>.

In conclusion, combining the theoretical results on the spin distribution and vibrational analysis, it is most likely that the Ag + SiO adduct observed in both the IR<sup>1</sup> and ESR<sup>3</sup> experiments has a bridge structure. This is the same structure proposed from the force-field analysis of the IR vibrations.<sup>1</sup> Although the linear structure reported earlier is also a stable isomer,<sup>2</sup> the atomic-like spin distribution and the virtually unchanged Si–O stretch do not fit the experimental observation as well. A bridge structure for AgSiO is not too surprising. Most transition metal–monoligand unsaturated hydrocarbon complexes favour the  $\pi$  (bridge) structure in accordance with the Dewar–Chatt–Duncanson model.<sup>8,9</sup> The experimental geometry for the adducts of ethylene with Cu<sup>10</sup> and Ag<sup>11</sup> are all found to have the bridge structure. This kind of chemical bonding is also well studied in main group metal–alkene complexes. The effects of electron correlation are often found to be crucial to the stability of the complexes.<sup>12–14</sup> The fact that previous theoretical work<sup>2</sup> did not locate the bridge structure does not contradict the findings reported here. The structure arrived from a geometry optimization depends critically on the initial geometry and the nature of the multidimensional potential energy surface. The interactions between the  $\pi$  system of SiO and Ag are expected to be small and the energy minimum of the bridge adduct would be quite shallow. This argument is supported by the observation that even when the optimization was started from a bent Si–O–Ag structure, the adduct settled into a linear structure.

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