

Transition-Metal Monosilyls [M(SiO), M = Cu, Ag, Au, V]: Electron Spin Resonance at 4 K

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Transition-metal monocarbonyls, M(CO), have been studied extensively both experimentally^{1–11} and theoretically.^{12–32} A logical next step is the investigation of the corresponding M(SiO) molecules (which we have named silyls here). CO and SiO are similar in that both have ¹Σ ground states with excited states lying above 30 000 cm⁻¹; however, their interatomic distances (*r*_e = 1.128 vs 1.510 Å) and dipole moments (−0.105 vs 3.088 D³³) are significantly different. The classic Dewar–Chatt–Duncanson model of the donation of CO 3σ orbital and back donation of the metal dπ orbitals is usually invoked in a qualitative discussion of bonding among carbonyls, but the bonding could be quite different in the silyls. Evidence indicates that all monocarbonyls are linear with the C bonded to the metal, but linearity is not assured in the monosilyls, nor perhaps is the bonding of the Si to the metal.

Mehner, Schnöckel, Almond, and Downs³⁴ were the first to study the coordination of SiO with transition-metal atoms. They assigned a band at 1163.0 cm⁻¹ to the Si–O stretching fre-

quency in Ag(SiO), red shifted by 63 cm⁻¹ relative to uncoordinated SiO. ^{28,29,30}Si and ^{16,18}O isotopic shifts indicated that the molecule is not linear but suggest that it has a triangular structure with the Ag–SiO angle ≤ 90°. There was also indication of the presence of a complex Ag(SiO)₂ or Ag_n(SiO)₂.^{35–37}

Electron-spin-resonance (ESR) spectra of ¹⁰⁷Ag plus SiO vapors in an adamantane matrix at 77 K were measured by Chenier, Howard, Joly, Mile, and Timms.³⁸ Apparently in that matrix the polymers (SiO)_n are readily formed so that the spectra of four molecules were detected, all assignable to Ag(SiO)_n species. An isotropic doublet split by 1226 MHz with *g* = 2.0001 was tentatively assigned to ¹⁰⁷Ag(SiO). This ¹⁰⁷Ag (*I* = 1/2) hyperfine splitting (hfs) can be compared to 1682 MHz observed for both ¹⁰⁷Ag atoms and ¹⁰⁷Ag(CO) in adamantane matrices. The three other doublets in the spectrum had smaller splittings. From approximate spin density considerations, the authors favor a nonlinear structure for Ag(SiO).

The early theoretical treatment of Ag(SiO) by Quelch, Grev, and Schaefer³⁹ favored a linear structure with weak bonding and the unpaired electron largely on Ag. However, Tse⁴⁰ found that a bridge structure with the metal interacting with both ends of SiO is the more stable one.

Köppe and Schnöckel⁴¹ have also investigated Na(SiO) and K(SiO) in the IR in argon matrices and believe that the large red shift in the SiO stretching frequency, as found for Ag(SiO), provides evidence for ionic bent molecules such as Na⁺(SiO)⁻ and Ag⁺(SiO)⁻.

The most recent experimental work is that of Mehner, Köppe, and Schnöckel⁴² who observed the IR spectrum of Pd(SiO) in an Ar matrix and from the ¹⁸O shift deduced a linear Si-bridged Pd–Si–O molecule. This was supported by *ab initio* calculations, which in fact suggested σ donor and π acceptor components in the bonding, as in PdCO, but in different proportions.

We observe the ESR spectrum of Ag + SiO but in the rare-gas matrices Ne and Ar at 4 K. Cu(SiO) and Au(SiO) have also been prepared; line shapes in the latter indicate clearly a nonlinear molecule. Then a search was made for other transition-metal (TM) monosilyls by vaporizing most of the first row TMs with SiO; only the spectrum of V(SiO) was observed.

The Heli-tran, ESR spectrometer, and laser vaporization apparatus have been previously described.⁴³ Two arrangements were used: (1) SiO solid (Apache Chemicals, 99.99%) was vaporized from a resistively-heated tantalum cell; (2) metal and SiO were vaporized simultaneously by a slightly defocused laser beam hitting both solid surfaces. Ar or Ne was used as matrix gases at 2–5 mmol/h. Deposition onto a Cu rod at ~4 K lasted 10 min if Ne was the matrix gas or 30 min if Ar was the matrix gas.

Cu(SiO): The ESR spectrum of ⁶³Cu (*I* = 3/2, enriched to 99.72%) plus SiO in an argon matrix at 4 K was observed centered at ~*g*_e including strong atom lines.⁴⁴ Analysis via an 8 × 8 spin matrix of the four isotropic lines displaying rather large second-order shifts and assuming *g*_{||} = *g*_e gave the almost isotropic magnetic parameters in Table 1. Comparison with the free atom *A*_{iso} = 5995 MHz^{45,46} yields 71% s character for the unpaired spin on Cu. There is no evidence of a nonlinear

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Table 1. Derived Magnetic Parameters for $M(\text{SiO})_n$ Molecules

	g_{\parallel}	g_{\perp}	A_{\parallel}^c	A_{\perp}^c	matrix	
$^{63}\text{Cu}(\text{SiO})$	2.0023 ^a	2.0020(5)	4235(5)	4239(5)	argon	
$^{107}\text{Ag}(\text{SiO})^b$	1.9937(10)	2.0024(10)	1361(5)	1365(5)	argon	
	1.9940(10)	2.0027(10)	1365(5)	1373(5)	neon	
$^{51}\text{V}(\text{SiO})$		1.9700(10)	463(20)	326(5)	argon	
$^{107}\text{Ag}(\text{SiO})_{2 \text{ or } 3}$		1.9993(5)	897(10)	876(5)	argon	
		1.9993(5)	924(10)	901(5)	neon	
	g_x	g_y	g_z	A_x	A_y	A_z
$^{197}\text{Au}(\text{SiO})^d$	1.9928(5)	1.9661(5)	1.9320(5)	1559(5)	1559(5)	1559(5)

^a Assumed. ^b Deduced from the more accurate ^{109}Ag results ($\mu_{107}/\mu_{109} = 0.8697$). ^c In MHz. ^d Argon matrix.

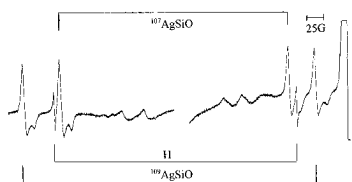


Figure 1. Expanded central portion of the ESR spectrum of natural silver plus SiO in an argon matrix at 4 K. Trapped H atoms produce the two sharp lines. Note the shapes of the Ag(SiO) lines and the four weak inner lines attributed to $\text{Ag}(\text{SiO})_{2 \text{ or } 3}$.

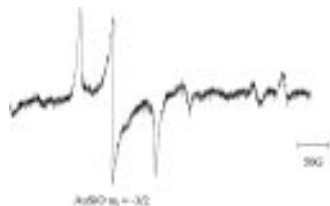


Figure 2. Expanded view of the ESR spectrum of Au plus SiO in an argon matrix at 4 K, near the line at ~ 4210 G. Note the distinct three g -valued shape of the $^{197}\text{Au}(\text{SiO})$ line.

structure from the line shapes. The Cu hyperfine (hf) anisotropy is very small $A_{\text{dip}} \cong -1(5)$ MHz, which when compared with an estimated free atom value of 200 MHz,² indicates that the remaining 29% of the spin is essentially on the SiO, although ^{29}Si hf was not observed. This result is similar to that found by Kasai and Jones³ for Cu(CO) where the s character was found to be 67% with 8% in the $4p\sigma$ on Cu and the remainder essentially on CO.² All theoretical studies^{13–30} of Cu(CO) indicate very weak bonding.

Ag(SiO): The ESR spectra of natural silver $^{107,109}\text{Ag}$ and SiO in argon and neon matrices were observed. An expanded view of the lines attributed to $^{107,109}\text{Ag}(\text{SiO})$ is shown in Figure 1. The strong atom lines⁴⁴ lie at lower and higher fields. Classic parallel and perpendicular features are evident, but there is no indication of a third g component which would show that the molecule is nonlinear (see Figure 2 for the Au(SiO) molecule). The four weaker inner lines are assigned to $\text{Ag}(\text{SiO})_{2 \text{ or } 3}$ (see below). Analysis yielded the magnetic parameters in Table 1. Like Cu(SiO), most of the unpaired spin is in an s orbital on the Ag atom: $|A_{\text{iso}}(^{107}\text{Ag})| = 1363$ MHz and $g_{\perp} \cong g_{\parallel} = g_e$. Comparison with the free atom $A_{\text{iso}} = 1831$ MHz yields 74% s character. The small anisotropy, $A_{\text{dip}} = -3(8)$ MHz, places 26% of the spin largely on the SiO adduct; thus $\text{Ag}(\text{SiO})$ is similar to the copper monosilyl. However, unlike Cu(SiO), the spectrum and magnetic parameters are quite different from the corresponding monocarbonyl. In Ag(CO), the percent s character is 99% so that the spin density on CO is almost negligible.³ Kasai and Jones suggest that the detected Ag(CO) in an argon matrix is a Ag atom and CO molecule separated by the nearest-neighbor distance of the host lattice. Our ESR spectrum implies much more overlap and in a clearly axial structure of a bonded $^2\Sigma$ molecule.

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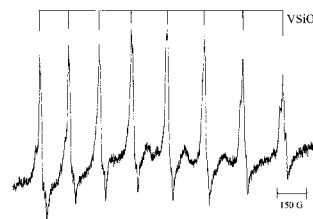


Figure 3. ESR spectrum of V plus SiO in an argon matrix at 4 K.

Table 2. Comparison of the Isotropic Hyperfine Coupling Constant (A_{iso}) and Percent s Character on the Metal Atom in the Monosilyls and Monocarbonyls

molecule	ground state	A_{iso} (MHz)	% s^a on metal	ref
$^{63}\text{Cu}(\text{SiO})$	$^2\Sigma$	4238	71	
Cu(CO)	$^2\Sigma$	4142	69	2, 6
$^{107}\text{Ag}(\text{SiO})$	$^2\Sigma$	1363	74	
Ag(CO)	$^2\Sigma$	1787	98	3, 5
$^{197}\text{Au}(\text{SiO})$	$S = 1/2$	1559	54	
Au(CO)	$^2\Sigma$	1705	59	4, 7
$^{51}\text{V}(\text{SiO})$	$^4\Sigma$	417	30	
V(CO)	$^6\Sigma$	177	21	9

^a Calculated from $A_{\text{iso}}/(\text{free atom } A_{\text{iso}})$. Free atom values (in MHz):⁴⁶ ^{63}Cu , 5995; ^{107}Ag , 1831; ^{197}Au , 2876; ^{51}V , (4165/3) or (4165/5).

Ag(SiO)₂ or 3: Similar to Chenier et al.,³⁸ we assign the four inner lines in Figure 1 to a larger SiO complex. Here $|A_{\text{iso}}(^{107}\text{Ag})| = 909$ MHz ($g_{\perp} \cong 1.9993$) which approximately corresponds to their molecule III in adamantane assigned to $\text{Ag}(\text{SiO})_2$: $A = 902$ MHz ($g = 1.9968$).³⁸

Au(SiO): An expanded view of one of the four hf lines of $^{197}\text{Au} + \text{SiO}$ in an argon matrix at 4 K (at 4210 G) is shown in Figure 2. Thus the g tensor is orthorhombic, establishing it as a bent $S = 1/2$ molecule, but both the g and A (^{197}Au) tensors are very isotropic (see Table 1). With $g_{\text{iso}} = 1.964$ and $|A_{\text{iso}}(^{197}\text{Au})| = 1559$ MHz, one finds, from the free atom value $A_{\text{iso}} = 2876$ MHz, that the s character is approximately 54% on Au with very little hf anisotropy. Kasai and Jones⁴ found that Au(CO) is linear with a similar percent s character.

V(SiO): The ^{51}V nucleus has $I = 7/2$ and is 99.8% naturally abundant. The spectrum in Figure 3 shows the eight hyperfine lines centered around 1700 G; the weak parallel lines lie upfield but were not observed. This corresponds to a $^4\Sigma$ molecule with a zero-field-splitting parameter $D \cong 2 \text{ cm}^{-1}$. Solution of the 32×32 spin matrix, assuming $D = 10 \text{ cm}^{-1}$, gave the parameters in Table 1. For positive hf components $A_{\text{iso}}(^{51}\text{V}) = 417$ MHz and $A_{\text{dip}}(^{51}\text{V}) = -46$ MHz, requiring the unpaired electrons to occupy $d\delta$ orbitals on vanadium. The three unpaired electrons on V in a nominal $so^1d\delta^2$ configuration, with $417/1388 = 30\%$ s hybridization, are reasonable since then $A_{\text{dip}} = 0.7/3 \times 2/7 \times 437.6 - 2/3 \times 2/7 \times 437.6 = -54$ MHz, where the free atom value for A_{iso} and A_{dip} are used.^{45,46} V(CO) is of higher spin, $S = 5/2$, than V(SiO), with a distinctly different spectrum.⁹ The two $d\pi$ electrons in the ground state configuration of that molecule are presumably bound to SiO in V(SiO) to lower the multiplicity from $^6\Sigma$ to $^4\Sigma$.

Table 2 sums up a comparison of ESR results for the monosilyls and monocarbonyls. Other first-row transition metals Sc, Cr, Mn, Fe, and Ni did not yield ESR spectra of $M(\text{SiO})_n$ molecules, but conditions should be varied before definitely ruling out their formation and/or detection of magnetic species. Of course, they would not be observed if their ground states are singlets [as is presumably the case for $\text{Pd}(\text{SiO})^4$] or, if linear, are orbitally degenerate (i.e., Π , Δ , etc.). Experimentally there is need for ^{29}Si (and ^{17}O) hf data using enriched isotopes and extension of these studies to other transition metals. Theoretical calculations are needed to understand the ground state bonding and structures as compared to the carbonyls.

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