under D_{2d} symmetry.

(25) G. L. Simon and L. F. Dahl, *J. Am. Chem. Soc.*, **95**, 2175 (1973).

(26) R. M. Roder and L. F. Dahl, submitted for publication.

(27) It is impossible to bookkeep in a straightforward fashion the particular MO-electronic configuration for the tetrairon cluster orbitals in the $[Fe_4(S_2C_2(CF_3)_2)_4(\mu_3\text{-}S)_4]^{2-}$ dianion due to the well-known ambiguity in electron assignment to the terminal dithiolene ligands which can function as radical anions.

SiCO, SiN_2, and $Si(CO)_2$ Molecules: Electron Spin Resonance and Optical Spectra at 4 K

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Received August 2, 1976

Abstract: The $^3\Sigma$ molecules carbonylsilene, SiCO, and diazasilene, SiNN, have been prepared by the vaporization and reaction of silicon atoms with N_2 or CO and trapped in various matrices at 4 K. Some or all sites in some matrices induced slight bending of the molecules. Isotopic substitution of ^{13}C, ^{18}O, ^{15}N, and ^{29}Si was employed to obtain hyperfine coupling data in the ESR and shifts in the optical spectra. In solid neon, assuming $g_\parallel = g_\perp = g_e$, D = 2.28 and 2.33 cm^{-1} for SiN_2 and SiCO, respectively. Hyperfine splittings confirm the CNDO calculated results which indicate that in both molecules the electron spins are largely in the pπ orbitals of Si. Optical transitions with vibrational progressions were observed beginning at 3680 and 3108 Å for SiN_2 and at 4156 Å for SiCO. IR spectra were obtained and stretching force constants calculated. An attempt was made to correlate these vibrational and electronic data with those for CCO and CNN. Annealing an argon matrix containing SiCO to 35 K led to the observation in the IR of $^1\Sigma$ $Si(CO)_2$, a silicon counterpart of carbon suboxide. A corresponding treatment of a SiN_2 matrix did not produce the N_2SiN_2 molecule, nor was the N_2SiCO molecule observed when both ligands were present.

Carbonylcarbene, CCO, and diazacarbene, CNN, are isoelectronic triplet molecules with distinctly different bonding[2-5] and zero-field-splitting (ZFS).[6,7] Also, although there is at present no evidence of a N_2CN_2 molecule, the carbon suboxide molecule, $C(CO)_2$, is quite stable and has been thoroughly studied. The triatomic species are readily formed by the reaction of carbon atoms with N_2 and CO at low temperatures, and here we report the investigation of their silene[8] counterparts. Although SiN_2, SiCO, and $Si(CO)_2$ can easily be produced and trapped in solid argon at 4 K, no evidence is found for the formation of the N_2SiN_2 molecule, in analogy with the instability of the corresponding carbon molecule.

A variety of matrices has been used here and all available stable isotopes of the four elements have been employed in clarifying the observed optical and ESR spectra. Apparently the two $^3\Sigma$ triatomic molecules are easily bent, and in the constraining sites of some solid matrices, this is detectable by ESR. There is, however, only evidence of linear molecules in the optical spectra, and, in fact, there is no evidence of progressions involving the bending frequency in any of the observed electronic transitions. Then, if any of the excited states are Π states, the Renner effect in the silenes must be much smaller than in the carbenes.

Experimental Section

The radicals SiCO and SiN_2 were prepared by the reaction of Si atoms with CO and N_2 in (Ar/CO) = (Ar/N_2) = 100–200, pure N_2, or pure CO matrices. A beam of Si atoms was vaporized from a tantalum cell at temperatures that varied from about 1500 to 1900 °C. Both resistance heating and induction heating were used. A Ta resistance cell (0.25 in. o.d. and 0.040 in. wall thickness) was used, which withstood the destructive Si–Ta alloying for several runs. The induction cell (Ta, ⅛ in. wall thickness) and furnace have been described previously.[9] The Si atoms were condensed simultaneously with a stream of matrix gas on either a CsI window, a CaF_2 window, or a sapphire rod maintained at 4 K.

In two experiments 95% enriched ^{29}Si powder (Oak Ridge National Laboratory) was mixed with an equal part of natural abundance Si (6-9's purity, SPEX Industries, Inc.) and vaporized from a resistance-heated cell. Isotopically enriched samples of $^{13}C^{16}O$ (Merck, Sharpe and Dohme of Canada, Ltd., 92.6 atom % enriched), $^{12}C^{18}O$ (Miles Laboratory, 96.88 atom % enriched), and $^{15}N_2$ (Merck, Sharpe and Dohme of Canada, Ltd., 95.0% enriched), were used in addition to $^{12}C^{16}O$ and $^{14}N_2$ (Airco, ultrapure grade). The rare gases, neon and argon, were Airco ultrapure grade and were used without further purification except for passage through a liquid nitrogen trap prior to deposition.

Optical spectra in the 2000–7500 Å range were recorded using a Jarrell-Ash 0.5m Ebert scanning spectrometer with gratings blazed at 5000 and 10 000 Å and utilizing either an RCA 1P21 or 7200 photomultiplier tube. A Perkin-Elmer 621 spectrophotometer was used in the infrared from 300 to 4000 cm^{-1}. ESR measurements were made with an X-band Varian model 4500 spectrometer with superheterodyne detection[10] with the magnetic field measured using a Walker Magnion gaussmeter. When the signals were weak a signal averager (Nicolet Model 1072 with SW-71A and SD-72A units) was used to improve the signal-to-noise ratio. The experimental apparatus has been previously described in detail.[10,11]

ESR Spectra

Theory. The spin Hamiltonian for a molecule with S = 1 can be written

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + D(S_z{}^2 - \tfrac{2}{3}) + E(S_x{}^2 - S_y{}^2) + \sum_i [A_\parallel{}^i I_z{}^i S_z + A_\perp (I_x{}^i S_x + I_y{}^i S_y)] \quad (1)$$

where D and E are the zero-field-splitting (ZFS) constants. The superscript i denotes a nucleus with a magnetic moment. The solution to this Hamiltonian, neglecting hyperfine (hf) interactions, is given by Wasserman et al.[12] Four lines are expected in the present case with the microwave field perpendicular to the static magnetic field (H) and $D > h\nu$:

$$H_{z_1} = [(h\nu - D)^2 - E^2]^{1/2}/g_\parallel \beta \quad (2)$$

$$H_{z_2} = [(h\nu + D)^2 - E^2]^{1/2}/g_\parallel \beta \quad (3)$$

$$H_{x_2} = [(h\nu + D - E)(h\nu - 2E)]^{1/2}/g_\perp \beta \quad (4)$$

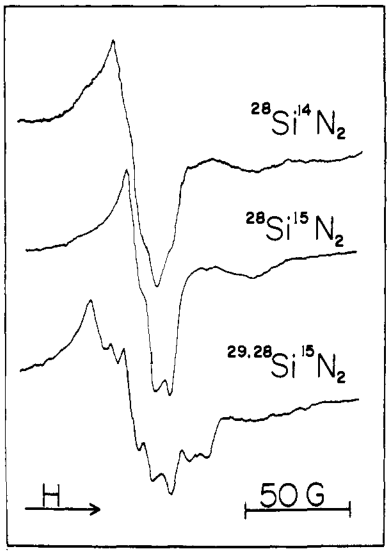

Figure 1. ESR spectra of SiN_2 molecules in argon matrices at 4 K. Line positions and microwave frequencies are given in Table I.

$$H_{y_2} = [(h\nu + D + E)(h\nu + 2E)]^{1/2}/g_\perp\beta \qquad (5)$$

When $E = 0$ (linear molecule), there are the three resonances for $D > h\nu$: eq 2-3 and

$$H_{xy_2} = [h\nu(h\nu + D)]^{1/2}/g_\perp\beta \qquad (6)$$

For $E < 0.009$ cm^{-1}, D may be obtained from the H_{x_2} and H_{y_2} resonances from

$$D = (g_\perp{}^2\beta^2/2h^2c\nu)\,[H_{x_2}{}^2 + H_{y_2}{}^2 - 2(h\nu/g_\perp\beta)^2] \qquad (7)$$

In the presence of a magnetic nucleus[13] with hf constants, A, small with respect to $g\beta H$, the splitting may be assumed to be

$$\Delta H_{z_1} = \Delta H_{z_2} = A_\parallel/g_\parallel\beta \qquad (8)$$
$$\Delta H_{xy_2} = A_\perp/g_\perp\beta$$

with less than 1% error.[7]

SiN_2. When silicon vapor is trapped in an argon matrix containing $^{14}N_2$ (M/A = 100) the strong line shown in Figure 1 (top) appeared at 9503 G in the ESR. (All ESR line positions were measured according to the criterion of Wasserman et al.[12]) A small triplet hf splitting of 6.0 ± 1 G due to interaction with one ^{14}N ($I = 1$) nucleus is discernible. Also a broad weak feature at about 50 G upfield appears and does not disappear after several annealing cycles between 25 and 4 K. The weak band is due either to a few linear molecules in alternate sites in the matrix or to some slightly bent molecules in the matrix (an E term in the spin Hamiltonian). As will be seen below, these weak bands appear in most, but not all, matrices and always appear at high fields relative to the large x_2 line. This suggests that in some sites, the matrix may induce the molecule to be slightly bent, particularly in molecules where the bending force constant is small, as may be the case for SiN_2.

Then the strong line is assigned as the xy_2 perpendicular line of a linear $^3\Sigma$ Si-N-N molecule and the weaker broad line to a y_2 perpendicular line of the small population of molecules which are slightly bent in their sites. For the linear molecule, assuming $g_\perp = g_e$, one then finds $D = 2.206$ cm^{-1} in argon, and for the bent molecules $D = 2.214$, $E = 0.000\,87$ cm^{-1}. Substitution of $^{15}N_2$ (95% enriched) yielded the spectrum in Figure 1 (middle) where the ^{15}N ($I = \frac{1}{2}$) doublet splitting is found to be 7.4 ± 1 G and again only the hf interaction with one ^{15}N nucleus was resolved. This also proves that the nitrogen atoms are not symmetrically disposed about the Si. This value yields 5.3 G for the ^{14}N hfs when multiplied by the gyromagnetic ratio factor $\gamma_{14}/\gamma_{15} = -0.713$, which is in satisfactory agreement with the observed value for $Si^{14}N_2$.

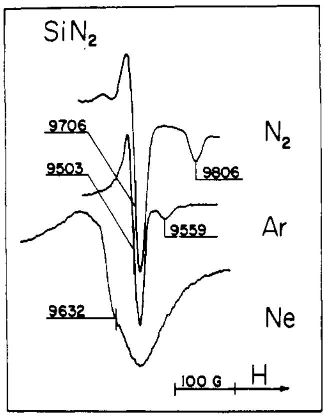

Figure 2. ESR spectra of SiN_2 molecules in various matrices at 4 K. Data are given in Table I.

Finally when an equal mixture of ^{28}Si and ^{29}Si ($I = \frac{1}{2}$) was trapped with $^{15}N_2$ the spectrum shown in the bottom of Figure 1 was obtained. This exhibits both the $^{28}Si^{15}N_2$ spectrum (Figure 1, middle) and a doublet of doublets due the ^{29}Si hfs of 34 ± 1 G.

When trapped in neon, $^{28}Si^{14}N_2$ exhibited a much broader line at 9632 G with no evidence of a weak y_2 line at higher field, as shown in Figure 2. The half-width of the neon line was 56 G as compared to 12 G in argon. (The half-line-width here is measured between the field at which the derivative ESR signal crosses the zero line and the field at the negative peak.) On one occasion a narrow line (~19 G wide) at 9624 G was observed on the low field side of the broad neon line with its peak about 50 G lower in field than the peak of the broad line. (This same shape was seen for SiCO in neon.) On other broad neon lines there was only an indication of a shoulder on the low-field side.

In a pure N_2 matrix it appears that most of the molecules are bent since a strong y_2 line of characteristic shape appears at 9806 G as shown in Figure 2. The entire spectrum is shifted upfield by about 200 G relative to that measured in an argon matrix; i.e., the D value increases to 2.343 cm^{-1} and $E = 0.001\,52$ cm^{-1}.

A search of the region where one might expect the z_1 and z_2 lines, assuming $g_\parallel = g_e$ and the observed D value, yielded no signals in all matrices even after signal averaging. This is not unusual for linear triplets since these lines are very weak and broadened by motional effects.[14] A summary of the D and E values derived from the spectra of SiN_2 in various matrices is given in Table I.

SiCO. Similar experiments with ^{28}Si, ^{29}Si, ^{12}CO, and ^{13}CO yielded the ESR spectra shown in Figure 3. For $^{28}Si^{12}CO$, an x_2 line with half-width of 5 G (as defined above) was obtained at 9488 G with a y_2 line at 9627 G, as measured at the points indicated in Figure 3 (top). A broad very weak line appears between the two at about 9584 G. Substitution of ^{13}CO causes only line broadening as in Figure 3 (middle), indicating that the ^{13}C hf is <~5 G. These lines are about twice as wide as those for ^{12}CO and their positions are shifted about 3 G to high field. Assuming $g_\perp = g_e$, one then obtains $D = 2.236$ cm^{-1} for $Si^{12}CO$ and 2.237 cm^{-1} for $Si^{13}CO$ with $E = 0.00215$ cm^{-1} for both. An intensive search for z lines at the predicted magnetic field values in the range of our magnet yielded no other resonances.

A 50:50 mixture of ^{29}Si and ^{28}Si yielded the spectrum in Figure 3 (bottom) where one sees the hfs clearly for both the x_2 and y_2 lines. The A(^{29}Si) value for the x_2 lines is 30 ± 1 G

Table I. ESR Data of SiN_2 and SiCO in Their $^3\Sigma$ Ground States in Various Matrices at 4 K

Molecule	Matrix	x_2 or xy_2 line (G)[a]	y_2 lines (G)	x_2 line half-width (G)[b]	ν(GHz)	D (cm^{-1})[c]	E (cm^{-1})[c]	$A_\perp$(G)
$Si^{14}N_2$	Ar	9503	(~9559)	12	9.3900	2.206	(0.000 87)	6.0 ± 1 (^{14}N)
	Ne	9632		56	9.3890	2.276		
	N_2	9706	9806	15	9.3880	2.343	0.001 52	
$Si^{15}N_2$	Ar	9509			9.3910	2.209		7.4 ± 1 (^{15}N)
	Ne	9632			9.3890	2.276		
$^{28,29}Si^{15}N_2$	Ar				9.3895			34 ± 1 (^{29}Si)
$Si^{12}CO$	Ar	9488	(~9584), 9627	5	9.3890	2.236	0.002 15	
	CO	9863		38	9.3865	2.402		
$Si^{13}CO$	Ar	9491	(~9588), 9630	10	9.3900	2.237	0.002 15	<5 (^{13}C)
	Ne	9720		70	9.3910	2.333		
$^{28,29}SiCO$	Ar	9489	9627		9.3880	2.236	0.002 15	30 ± 1 (^{29}Si)

[a] Line position determined by the criterion of ref 12. [b] Half-width is here measured between the field at which the derivative signal crosses the zero line and the field at the negative peak. [c] Calculated assuming $g_\perp = g_e = 2.0023$.

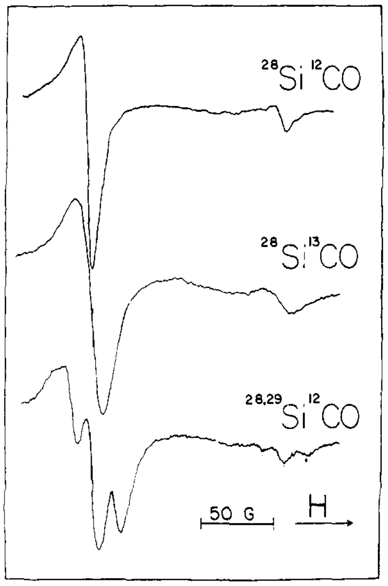

Figure 3. ESR spectra of SiCO molecules in argon matrices at 4 K. Line positions and microwave frequencies are given in Table I.

and that for the y_2 line is the same within the larger experimental error for the weaker line.

Several annealings to 20–25 K did not change the general pattern of the lines of SiCO near 9500 G when observed at 4 K. When the spectrum was measured at 25 K the spectrum changed from that at 4 K in Figure 4A to that in Figure 4B. The entire spectrum became much weaker, the high field lines apparently disappearing, and the x_2 line shifting 7 G to lower field, as would be expected for some motional averaging. Quenching to 4 K again gave the spectrum in A. Measurement of the spectrum at intermediate temperatures showed only a gradual diminution of the entire pattern and slight shifts to lower fields with increasing temperature until at 25 K the spectrum in Figure 4B was obtained.

As with SiN_2, trapping SiCO in neon at 4 K gave a much broader spectrum of the same shape as that shown in Figure 2. It appeared to also consist of a narrow line superimposed on the low field side of a broad line of width about 70 G.

In pure CO the spectrum obtained is shown in Figure 5. It is much broader than in argon and has a feature at low field not observed in other spectra. Neither this nor the shoulder on the high field side of the main line was removed by annealing.

The D and E values for SiCO in the various matrices are also listed in Table I.

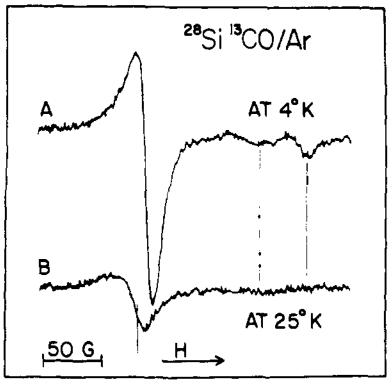

Figure 4. Effect of temperature upon the ESR spectrum of $Si^{13}CO$ in an argon matrix: (A) spectrum measured at 4 K; (B) spectrum measured at 25 K.

Si_2. Although Si_2, ground state $^3\Sigma_g^-$, is certainly present in most of the matrices as indicated by their ultraviolet spectra (see below), it was not observed in the ESR spectra. Its ZFS must then have a lower limit of about 4 cm^{-1} in order to put its xy signal outside of the range of magnetic fields available here.

Optical Spectra

Si and Si_2. The mass spectrometric work of Honig[15] has established that atomic silicon is the predominant vapor species over hot silicon and that Si_2, Si_3, and Si_4 are present in about 1 to 2%. Although Si and Si_2 often appear strongly in the optical matrix spectra, no bands attributable to other pure silicon molecules were detected, even after warming to allow some diffusion to occur. Two strong broad bands at 2320 Å (43 090 cm^{-1}) and 2190 Å (45 648 cm^{-1}) and a weaker one at about 2270 Å (44 039 cm^{-1}) in argon matrices appear to be due to Si atoms. In the gas phase one strong line, originating from the ground state, is observed at 2514.32 Å (39 760 cm^{-1}, $^3P_1{}^0 \leftarrow {}^3P_0$) and a weaker line at 2207.97 Å (45 276 cm^{-1}, $^3D_1{}^0 \leftarrow {}^3P_0$).[16,17] In general, atomic transitions are blue shifted and sometimes split in matrices,[18] and this also seems to hold here. Although no definite assignment can be made, it appears that the two strong matrix bands correspond to the two gas transitions with $\nu_{Ar} - \nu_{gas}$ shifts of +3330 and +370 cm^{-1}.

The Si_2 spectrum is also well known[19] and has been observed in matrices.[20,21] On occasion, extensive progressions of the Si_2 H ← X (4021–3562 Å) and K ← X (3257–3011 Å) were observed here in solid argon. In Table II they are compared with those reported by Milligan and Jacox.[20] The latter were prepared by photolysis of various silanes in argon matrices and

Table II. Si_2 Absorption Bands in Argon Matrices at 4 K

This work		Milligan and Jacox[b]	
ν (cm^{-1})[a]	$\Delta\nu$	ν (cm^{-1})	$\Delta\nu$
	H ← X		
24 863		24 937	
	311		213
25 174		25 150	
	234		275
25 408		25 425	
	273		261
25 680		25 686	
	239		267
25 920		25 953	
	274		252
26 194		26 205	
	227		243
26 421		26 448	
	265		225
26 686		26 673	
	232		237
26 918		26 910	
	236		256
27 153		27 166	
	231		
27 384			
	236		
27 621			
	211		
27 831			
	235		
28 066			
	K ← X		
30 694		30 647	
	449		448
31 143		31 095	
	435		442
31 578		31 537	
			413
		31 950	
32 414			
	398		
32 812			
	390		
33 202		33 213	
			368
		33 581	
			400
		33 981	
			397
		34 378	

[a] Estimated error = ±15 cm^{-1}. [b] From data on photolyzed SiH_4 in an argon matrix in Table II of ref 20.

the differences probably lie within the uncertainty in the measurements of band peaks. The D ← X system was not identified in our matrices, perhaps because it was usually overlapped by a stronger, unidentified, progression with a spacing of about 870 cm^{-1}. This latter system was produced in varying intensity when silicon was evaporated from a tantalum cell and trapped in argon. It may be due to the Si-Si-O molecule since oxygen is a known impurity in tantalum metal, and the SiO $^1\Pi \leftarrow X^1\Sigma$ transition was often observed between 2100 and 2300 Å in the matrix spectra.

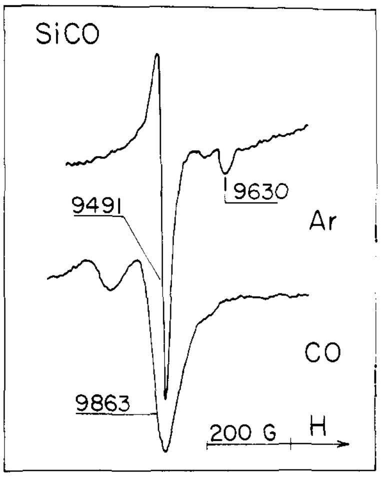

Figure 5. ESR spectra of SiCO molecule in Ar and CO matrices at 4 K.

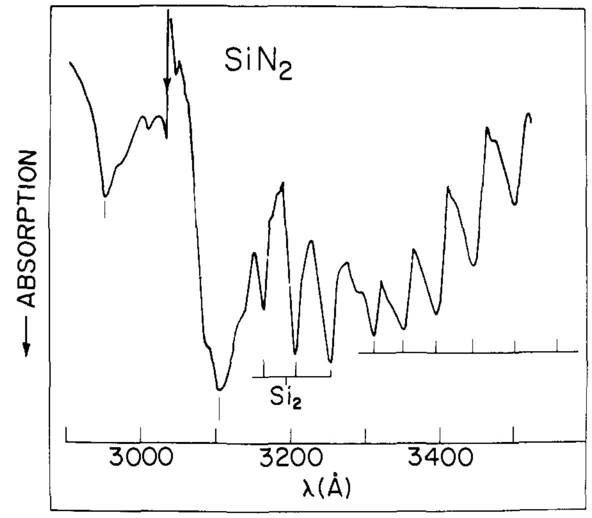

Figure 6. Ultraviolet absorption spectrum of SiN_2 molecules in an argon matrix at 4 K. (Arrow indicates increase in slit width.)

SiN_2. A progression of bands separated by about 450 cm^{-1} was observed beginning at about 3680 Å when Si vapor was deposited in a $N_2/Ar = 200$ matrix, as indicated in Figure 6. The first three observed members of the progression are not shown in that figure, but the large anharmonicity in the higher members is clearly evident. Also attributed to SiN_2 are two large single bands at 3109 and 2955 Å, separated by 1670 cm^{-1}. This spacing is about what might be expected for the N-N stretching frequency in the excited state, but it is not definite that these two bands belong to the same electronic transition since a third band at about that spacing could not be found. However, the shapes of these bands are similar, and the rapidly decreasing intensity of that at 2955 Å suggests that the Franck-Condon factors are changing rapidly.

Unfortunately the substitution of $^{15}N_2$ did not establish the assignments. The vibrational frequency of about 450 cm^{-1} (presumably the Si-N stretching frequency) in the first system did not shift very much when the heavier isotope was substituted, and the N-N stretching frequency does not appear in that system. The breadth of the bands also made their exact position uncertain. A similar problem arose with the second system.

Then we tentatively assign these bands to two electronic transitions as shown in Table III. The (0,0,0) band of the system at 3680 Å cannot be definitely specified and could lie at longer wavelengths.

The SiN_2 spectrum was also observed, along with that of SiO, Si_2O(?), and Si_2, when N_2O was used as the reactive gas rather than N_2.

Observed IR bands are shown in Figure 7. The $^{15}N_2/Ar$ spectrum is similar but slightly shifted relative to the $^{14}N_2$

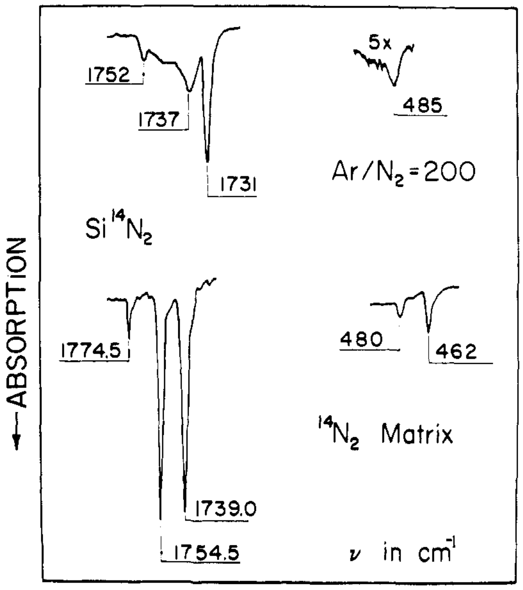

Figure 7. Infrared bands of SiN_2 in argon (upper) and nitrogen (lower) matrices at 4 K.

Table III. Ultraviolet Absorption Spectrum of $Si^{14}N_2$ in an Argon Matrix at 4 K

v'[a]	λ' (Å)[b]	ν' (cm^{-1})[b]	$\Delta G_{v'+1/2}$ (cm^{-1})
		A ← X System	
0	~3680	~27 170	
			~430
1	3622	27 600	
			470
2	3562	28 070	
			470
3	3503	28 540	
			453
4	3448	28 993	
			431
5	3398	29 424	
			401
6	3352	29 825	
			353
7	3313	30 178	
		B-X System	
0	3108.4	32 162	
			1672
1	2954.7	33 834	

[a] The v' values assigned to the A ← X system could be low since the (0,0) band may have been too weak to be observed. [b] Averages of measurements on two spectra. Estimated errors are ±3 Å and ±20 cm^{-1} in the A-X system and ±1 Å and ±10 cm^{-1} in the B-X system.

spectrum given there. The splittings in the two observed bands are attributed to matrix effects. Then, in argon, the vibrations are assigned as ν_3(Si-N) 485 and ν_1(N-N) 1731 cm^{-1} for a linear molecule. These values, combined with the $^{15}N_2$ data in Table IV, yield the stretching force constants f_{NN} = 11.83 and f_{SiN} = 2.02 mdyn/Å, indicating a weak SiN bond. The bending frequence was not observed.

The vibrational frequencies in the excited states are in accord with decreasing bonding in the N-N and SiN bonds in these two electronic transitions. In neither transition is there an indication of a progression in a bending frequency.

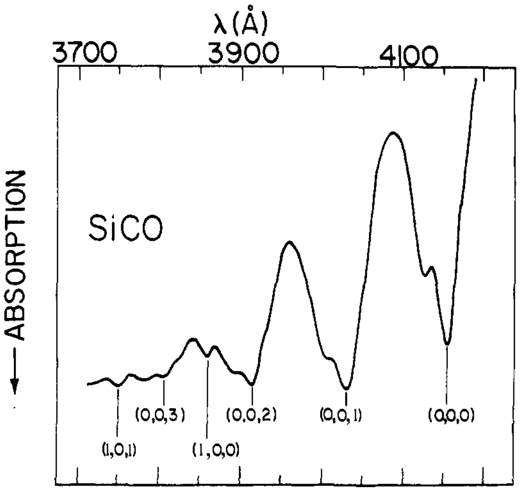

Figure 8. Absorption spectrum of SiCO molecules in an argon matrix at 4 K.

Table IV. Vibrational Frequencies and Calculated Force Constants (mdyn/Å) for SiNN and SiCO Molecules in Their Ground $^3\Sigma$ States

SiNN $f_{Si\text{-}N}$ = 2.021, $f_{N\text{-}N}$ = 11.825
SiCO[a] $f_{Si\text{-}C}$ = 5.3, $f_{C\text{-}O}$ = 15.6, $f_{SiC\text{-}CO}$ = 2.4

	Frequency (cm^{-1})			
	ν_1		ν_3	
Molecule	Obsd	Calcd	Obsd	Calcd
28-14-14	1731	1732.6	485	484.1
28-15-15	1676	1674.2	475	475.9
28-12-16	1899.3	1899.3	(800)[a]	800.0
28-13-16	1855.3	1855.4		793.7
28-12-18	1856.4	1856.5		785.3

[a] Si-C stretching frequency in $Si^{12}C^{16}O$ was assumed to be 800 cm^{-1} since it was not observed but inferred from the value in the excited state (see text).

SiCO. The absorption spectrum of this molecule is shown in Figure 8. It begins at 4160 Å and exhibits a progression with spacing of about 750 cm^{-1}. A second progression appears to begin at 3860 Å indicating that another vibrational frequency, 1857 cm^{-1}, is also excited in the upper electronic state. All bands have a shoulder on the high frequency side which may be due to matrix effects, possibly phonon interactions.[22] The observed bands and their assignments are given in Table V. No other electronic transitions of SiCO were observed between 8000 and 2000 Å.

In the IR spectra of argon matrices only the C-O stretching frequency at 1899.3 cm^{-1} could definitely be identified as belonging to SiCO (see Figure 9A). Considerable effort was expended to observe a Si-C stretching frequency below 1000 cm^{-1}, but no band was detectable in neon or argon matrices which could be assigned to SiCO. A matrix was also made by vaporization of Si into pure ^{12}CO and a large IR band at 1909 cm^{-1} indicated that it contained a high concentration of SiCO. (This was partially confirmed when this band disappeared completely after the matrix was annealed to 40 K (see below).) Reasoning from the electronic spectra of SiCO, one expects the Si-C frequency in the ground state to lie above and near 750 cm^{-1}. A very weak band did appear at 803 cm^{-1} in the CO matrix, but it cannot be definitely assigned to SiCO. The observed vibrational frequencies and force constants calculated assuming $\nu_3'' \cong 800$ cm^{-1} are given in Table IV.

$Si(CO)_2$. As opposed to N_2, CO is observed to form a linear $Si(CO)_2$ molecule. This is shown most clearly in the IR spectra in Figure 9. Here a mixture of equal parts of ^{12}CO and ^{13}CO

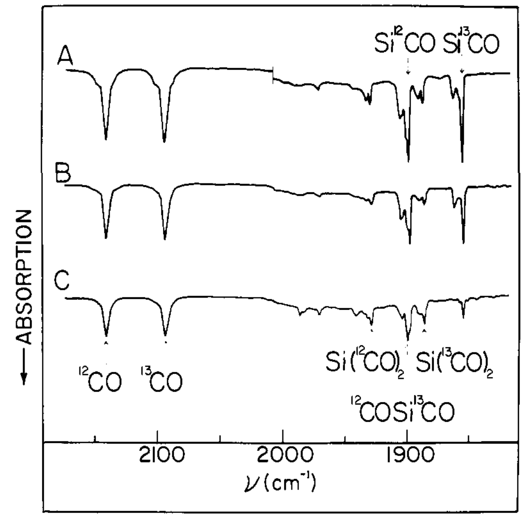

Figure 9. Infrared spectra at 4 K of an argon matrix containing vaporized silicon atoms and $^{13}CO/Ar = ^{12}CO/Ar = 1/375$: (A) initial spectrum, (B) spectrum after warming to 15 K and cooling to 4 K, (C) spectrum after warming to 35 K and cooling to 4 K.

Table V. Absorption Spectrum of Si^{12}CO in an Argon Matrix at 4 K

(v_1', v_2', v_3')	λ' (Å)[a]	ν' (cm^{-1})[a]	$\Delta\nu_3'$ (cm^{-1})	$\Delta\nu_1'$ (cm^{-1})
(0,0,0)	4155.7	24056		
	(4128.0)[b]	(24218)		
			750	
(0,0,1)	4030.2	24806		
	(4007.0)	24949)		
			737	1857
(0,0,2)	3913.9	25543		
	(3892.7)	(25682)		
			726	
(0,0,3)	3805.7	26269		
(1,0,0)	3858.0	25913		
			751	
(1,0,1)	3749.3	26664		
			724	
(1,0,2)	3650.2	27388		

[a] Maximum estimated error is ±1 Å and ±10 cm^{-1}. [b] Bands in parentheses are the shoulders on the high frequency sides of the strongest bands (see Figure 8).

in argon was reacted with Si to yield the two strong bands of Si^{12}CO and Si^{13}CO at 1899.3 and 1855.3 cm^{-1}, respectively (Figure 9A). Annealing to successively higher temperatures then gave the spectra in Figures 9B and 9C where it is seen that the SiCO bands decrease in intensity and are replaced by three bands at 1928, 1899.6, and 1886 cm^{-1} with the middle one stronger than the other two. These bands are attributed to the formation of OCSiCO, the counterpart of carbon suboxide, where the middle band is assigned to the mixed molecule O^{13}CSi^{12}CO. Again, no bands at lower frequencies could be definitely assigned to these molecules.

Figure 10 shows a similar IR spectrum when a mixture of $^{12}C-^{16}O$ and $^{12}C-^{18}O$ in argon was used as the matrix. Three C-O stretching frequencies are here observed to occur at 1928, 1897.5, and 1882.5 for Si(C^{16}O)$_2$, Si(C^{16}O)(C^{18}O), and Si(C^{18}O)$_2$, respectively.

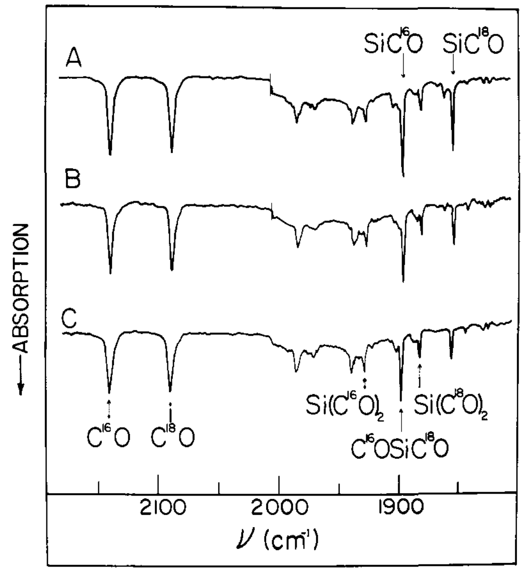

Figure 10. Infrared spectra at 4 K of an argon matrix containing vaporized silicon atoms and $C^{18}O/Ar = C^{16}O/Ar = 1/375$: (A) spectrum after initial matrix was warmed to 20 K and cooled to 4 K, (B) after warming to 30 K and cooling to 4 K, (C) after warming again to 30 K and cooling to 4 K.

Table VI. Comparison of Stretching Force Constants (mdyn/Å) for Relevant Molecules XYZ

Molecule	f_{xy}	f_{yz}
CNN[a]	19.5	14.7
SiNN	2.0	11.8
CCO[b]	6.0	14.9
SiCO[c]	5.3	15.6
C(CO)$_2$[d]	11.8	15.4
SiCC[e]	7.4	8.0
C$_3$[f]		10.3

[a] Interaction force constant = 3.9, ref 3. [b] Interaction force constant = 1.4, ref 2, 4. [c] ν_3 assumed to be 800 cm^{-1} (see Table IV and text). [d] Reference 23. [e] Reference 21. [f] Interaction force constant = 0.54, ref 36. (See ref 24 for a summary of C$_3$ data.)

Discussion

Since for SiCO, the Si-C stretching frequency was not detected in the IR, we have assumed that it lies near 800 cm^{-1} because of the observed value of 750 cm^{-1} in the excited state. On that basis the stretching force constants in Table IV were calculated. Both frequencies were detected for SiN$_2$ so that there was no ambiguity there and an adequate fit to the data for two isotopically substituted molecules could be made assuming the interaction force constant was zero.

Then, although the Si-C force constant in the ground state of SiCO can only be inferred from the spectral data obtained here, both the Si-C and C-O bonds appear to be quite strong, with the latter frequency in the range found for transition metal carbonyls. Just the opposite is true of SiN$_2$ where the Si-N force constant is low (2.02 mdyn/Å) and the N-N force constant is considerably decreased from that in the transition metal complexes. Comparison of force constants in related linear molecules is given in Table VI.

In their review of N$_2$ complexes of the transition metals, Allen et al.[25] have considered the bonding found there and compared it with that of CO. It is interesting to note that the Si-N$_2$ stretching frequency of 485 cm^{-1} is in the range of 450-550 cm^{-1} assigned to the M-N$_2$ frequencies, but $\nu(N_2)$ is lowered by about 600 cm^{-1} (the free N$_2$ frequency is 2330 cm^{-1}) as opposed to 100-400 cm^{-1} in the transition metal complexes. It is also understandable that CO with its suggested stronger π-acceptor and σ-donor orbitals[26] could bond twice

Table VII. Spin Densities in SiCO and SiNN

SiCO				$SiN_{\alpha}N_{\beta}$			
		Obsd[a]	Calcd[b]			Obsd[c]	Calcd[d]
Si	$p\pi$	0.74	0.657	Si	$p\pi$	0.84	0.939
	$d\pi$		0.015		$d\pi$		0.000
C	$p\pi$	<0.13	0.030	N_{α}	$p\pi$		−0.061
O	$p\pi$		0.298	N_{β}	$p\pi$	0.30	0.122

[a] Hfs from Table I divided by 40.7 G for ^{29}Si and 38.2 G for ^{13}C (from ref 32). Here all observed spin density on Si has been assumed $p\pi$. [b] CNDO values at energy minimum where $r_{Si-C} = 1.8$ Å, $r_{C-O} = 1.21$ Å. [c] Hfs from Table I divided by 40.7 G for ^{29}Si and 19.8 G for ^{14}N (from ref 32). All observed spin density on nitrogen has here been placed on N_{β} to conform to the CNDO results. [d] CNDO values at energy minimum where $r_{Si-N} = 2.0$ Å, $r_{N-N} = 1.14$ Å.

with Si to form $Si(CO)_2$ while its counterpart was definitely not observed with N_2.

CNDO calculations substantiate these differences. From the density matrix elements, $P_{\mu\nu}$,[27] in a manner analogous to that of Olsen and Burnelle in their treatment of CCO,[28] one can compare total σ and $p\pi$ charge densities with those of the free ligands. One then finds that the increase in charge density from Si $p\pi$ back-bonding is seven times greater in SiCO than SiN_2 while σ donation leading to a decrease in charge density is 2.3 times greater in SiCO. d-Orbital participation, while small in both molecules, is larger in SiCO than in SiN_2.

From the ESR data it appears that SiN_2 and SiCO molecules are bent in some sites in some matrices. SiN_2 in a pure N_2 matrix and SiCO in argon were cases where almost all molecules appeared to be nonlinear, judging from the relative intensities of the x_2 and y_2 lines. CNDO calculations on the two molecules confirmed that small departures from linearity can be expected to be unstable with respect to the linear conformation. Then the inference is that the molecular bending force constant is quite low and the constraints in the matrix sites induce bending.[29] Wasserman et al. had similarly observed a spectrum of a bent triplet molecule when observing the ESR of C_3N_2 in a hexafluorobenzene matrix,[6] and they interpreted it in the same way. The low bending frequency of that molecule[30] makes it a reasonable assumption, and it also seems reasonable here. The bending frequency in SiC_2 is 147 cm^{-1}, and it is probably even lower in SiCO.

It is also clear that there are motional effects upon the ESR spectra in the various matrices. In neon, which is the least polarizable and usually the least perturbing matrix, the ESR signals are unusually broad, and presumably this stems from such effects, as, for example, occur so strongly for matrix-isolated O_2.[31]

Experimental and calculated spin densities are given in Table VII and are in essential agreement for SiCO and SiN_2. Observed hfs values were converted to approximate spin densities by dividing by the atomic data indicated in the table. Almost all unpaired spins in SiCO are on Si and O. Experimentally hf splittings due to only one N nucleus were observed in the ESR spectra of SiN_2 and the CNDO calculations indicate that this is N_{β} (as is also the case in CNN). However, the calculated spin density on N_{β} is considerably smaller than the experimental value. The CNDO calculations also indicate that the unpaired π electrons have very little d character in both molecules.

The D values for SiN_2 and SiCO are most reliably obtained from the neon matrix data, which probably provide a lower limit, with the gas-phase value perhaps 0.1 cm^{-1} higher.[7] From Table I, the neon values are 2.28 and 2.33 cm^{-1}, respectively, as compared to 1.16 and 0.74 cm^{-1} for CNN and CCO.[7] The larger D values for the silicon molecules are understandable because of the larger spin-orbit coupling constant of Si (75 cm^{-1}) compared to C (26 cm^{-1}). The relatively large spin density in the Si $p\pi$ orbitals in these molecules amplifies this spin-orbit contribution to D.[33] However, on this basis the question that does arise is why the ZFS for SiN_2 is not larger than that for SiCO, judging by the spin density distributions given in Table VII. One can conjecture that the spin-spin contribution to D may be smaller in SiN_2 than in SiCO, even though the spin-orbit contribution is larger. The reasoning is that the larger spin-spin contribution in SiCO arises because of the relatively large spin density on the small O atom, whereas the larger spin-orbit contribution arises in SiN_2 because of the greater spin density on the heavier Si atom.

The ground state configuration of SiCO and SiN_2 can be written, in analogy with C_2O[5] and CN_2, as ... $(4\sigma)^2(2\pi)^4(5\sigma)^2(3\pi)^2\ {}^3\Sigma^-$, where small contributions from d orbitals on Si may now enter into the molecular orbitals. The excited $^3\Pi_i$ state observed by Devillers and Ramsay[5] for C_2O at 8500 Å arises for the silicon molecules from the configuration ... $(4\sigma)^2(2\pi)^4(5\sigma)^1(3\pi)^3\ {}^3\Pi_i$, $^1\Pi$, and there were indications of vibronic mixing with an excited $^3\Sigma^-$ state which can now arise from the configuration ... $(4\sigma)^2(2\pi)^3(5\sigma)^2(3\pi)^3\ {}^3\Sigma^{\pm}$, $^{1,3}\Delta$, $^1\Sigma^{\pm}$. The optical data observed for all four molecules are summarized in Table VIII, which also includes the data for SiC_2[34] and C_3.[35]

For SiN_2, one would tend to associate the transition at 27 200 cm^{-1} with a $^3\Pi_i$ upper state and that at 32 200 with the $^3\Sigma$ excited state. This would associate the 470-cm^{-1} progression with a $3\pi \leftarrow 5\sigma$ electron excitation, weakening the Si-N

Table VIII. Comparison of Vibrational Frequencies and Electronic Transitions of CXY and SiXY Molecules

Electr state	Vibr mode	Vibrational frequency (cm^{-1})					
		SiN_2	CNN[a]	SiCO	CCO[b]	SiC_2[c]	C_3[d]
Ground	ν_1''	1 733	2 847	1 899	1 978	1 742	2 040
	ν_2''		393		379	147	63
	ν_3''	485	1 241	(800)	1 074	852	1 230
T_{00} (cm^{-1})		27 200[e]	23 800[g]	24 100	11 700	20 100	24 700
		32 200[f]					
Excited	ν_1'	1 670[f]		1 857	2 046	1 464	
	ν_2'		(340)[g]		608	145	308
	ν_3'	470[e]	(1 325)[g]	750	~1 270	499	1 086

[a] From ref 3 and 4. [b] From ref 5. Ground state $^3\Sigma^-$, excited state $^3\Pi_i$, Renner parameter $\epsilon = -0.172$. [c] from ref 34. Ground state $^1\Sigma$, excited state $^1\Pi$, Renner parameter $\epsilon = +0.023$. [d] From ref 35. Ground state $^1\Sigma$, excited state $^1\Pi$, Renner parameter $\epsilon = +0.537$. [e] Upper state possibly $^3\Pi_i$. [f] Upper state possibly $^3\Sigma$. [g] From ref 3 and 37. Ground state $^3\Sigma^-$, excited state assumed to be $^3\Pi_i$, Renner parameter ϵ probably near −0.17. (Note that for NCN $\epsilon = -0.168$, essentially the same as CCO.) ν_2' is derived here from the observed difference 596 cm^{-1} in ref 37, assuming $\epsilon = -0.17$.

bond, and the 1670-cm^{-1} "progression" with a $3\pi \leftarrow 2\pi$ excitation, weakening the N-N bond.

For SiCO the assignment is more difficult to guess since the transition energy is more than twice that of the $^3\Pi_i \leftarrow X^3\Sigma$ system of CCO, and therefore might not involve similar orbitals. However, as discussed for the SiC_2 molecule,[21] if substitution of Si for C can be expected to increase σ bonding at the expense of π bonding, the differences might be rationalized. Then for an increase in the π-σ energy, the transition energy would rise and the changes in vibrational frequencies in the two molecules during excitation might be expected to occur as in Table VIII, i.e., those of CCO all rising and those of SiCO all falling. This weakening of the π bonding upon substitution of Si for C is also expected in CNN, but presumably it is less drastic.

One difficulty with both of the $^3\Pi \leftarrow X^3\Sigma$ assignments is the lack of discernible multiplet triplets, split by perhaps 50-70 cm^{-1}, in the ultraviolet spectra. This must be rationalized as due to either unresolved structure hidden under the broad bands or to matrix effects leading to distortion and/or shifts in the multiplet components. The latter is prevalent in atomic spectra in matrices.

It is noteworthy that none of the upper-state progressions exhibits irregularities, indicating that if any of those states are indeed Π states, the Renner effect is small. This is in accord with the very large drop in the Renner parameter $\epsilon = +0.537$ in C_3[35] to $\epsilon = +0.023$ in SiC_2.[34]

SiC_2 and C_3 contain two less valence electrons than the other molecules in Table VIII, and their observed transition is $^1\Pi \leftarrow X^1\Sigma$, but it still involves the excitation of a 5σ (or 4σ) electron into an (empty) 3π (or 2π) orbital. All of the silicon molecules are self-consistent in that regard since excitation into the 3π orbital leads to a decrease in the observed vibrational frequencies in each molecule. The carbon molecules, on the other hand, appear to exhibit more irregularities.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research under Grant AFOSR 76-2906 and the National Science Foundation under Grant MPS 74-22991. The authors are grateful to Professor W. B. Person for allowing us access to Professor J. Overend's program, and to Dr. J. Newton for his aid in the computation of vibrational frequencies and force constants. The authors are also grateful to the Northeast Regional Data Center at the University of Florida for providing some computational support.

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