

A SEARCH FOR INTERSTELLAR SILICON NITRIDE

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ABSTRACT

We have searched for the $N = 2-1$ rotational transition of silicon nitride, SiN, at 87 GHz. Upper limits to the SiN column densities are $N_{\text{SiN}} \leq 10^{12}-10^{15} \text{ cm}^{-2}$. The ratios of the abundances of SiN to CN toward the four sources observed are $\text{SiN}/\text{CN} \leq 0.002-0.08$, significantly less than the silicon-to-carbon ratio of 0.1. These ratios suggest that either silicon is depleted onto grains where CN is present, or that ion-molecule chemistry does not favor the production of SiN. Upper limits to the SiN/SiO ratios are significantly less than the nitrogen-to-oxygen ratio for Orion-KL and IRC +10216, indicating that the chemistry responsible for producing SiO does not correspondingly produce SiN. We report detection of ^{30}SiS toward IRC +10216, and comparison with ^{28}SiS and ^{29}SiS yields terrestrial isotopic abundance ratios for silicon.

Subject headings: interstellar: abundances — interstellar: molecules — line identifications

I. INTRODUCTION

The study of interstellar silicon chemistry is both an interesting and demanding task. To date only two silicon-bearing molecules have been observed: SiO and SiS. These observations (e.g., Lada, Oppenheimer, and Hartquist 1978; Downes *et al.* 1982; Wright *et al.* 1983) and certain theories (e.g., Hartquist, Oppenheimer, and Dalgarno 1980; Watson and Walmsley 1982; Graedel, Langer, and Frerking 1982) suggest that molecules containing silicon may not be formed and maintained by the same gas-phase ion-molecule chemistry that prevails in dark clouds or quiescent molecular clouds, but rather by the chemistry associated with high temperatures and densities (and possibly grain evaporation or destruction) which may be present in shocked or energetic gas or in circumstellar shells. The limited spatial extent of the thermal SiO emission toward Orion-KL (Wright *et al.* 1983), the vibrationally excited and masing properties of both SiO (e.g., Snyder and Buhl 1975; Schwartz, Zuckerman, and Bologna 1982; Clemens and Lane 1983) and SiS (Henkel, Matthews, and Morris 1983), and the complete absence of both SiO and SiS from dark clouds are in sharp contrast to the characteristics of their carbon analogs, CO and CS. However, interpretation of the silicon molecular observations is not trivial; the masing properties of the many transitions of SiO mask determination of column densities, and emission from SiS is very weak.

Enlargement of the list of silicon-bearing molecules would greatly elucidate many of the unique aspects of the chemistry of this element. Recently, Saito, Endo, and Hirota (1983) have measured the microwave spectrum of SiN, obtaining accurate frequencies which enable an interstellar search for this molecule to be made.

Figure 1 shows the energy level diagram of SiN for the $N = 2$ and $N = 1$ rotational levels and their electric-dipole transitions. The ground state of SiN is $^2\Sigma^+$, a near Hund's coupling case $b_{\beta J}$, and exhibits spin-rotation as well as magnetic- and electric-quadrupole hyperfine interactions. The transitions between levels $(J, F) = (5/2, 7/2) - (3/2, 5/2)$ at 87.5598 GHz and $(5/2, 5/2) - (3/2, 3/2)$ at 87.5675 GHz exhibit 27% and 17% of the total intensity of the $N = 2-1$ transition,

respectively, while the transition $(3/2, 5/2) - (1/2, 3/2)$ at 87.0499 GHz contains 17% of the 2–1 intensity. These transitions are the strongest ones between $N = 1$ and 2.

We report the results of a sensitive search for the $N = 2-1$ transition of SiN, primarily the $J = 5/2-3/2$ multiplet, toward Orion-KL, IRC +10216, Sagittarius B2, and DR 21(OH), using the 14 m dish of the Five College Radio Astronomy Observatory (FCRAO) and one of the 6 m antennas at Hat Creek (UC Berkeley). We detected no lines attributable to SiN, obtaining stringent upper limits for the column densities. A new species of silicon sulfide, ^{30}SiS , was detected via its $J = 5-4$ transition. In the following sections, the equipment and observations are described and the results presented. The chemical implications of the SiN upper limits are discussed in comparison with CN and SiO abundances.

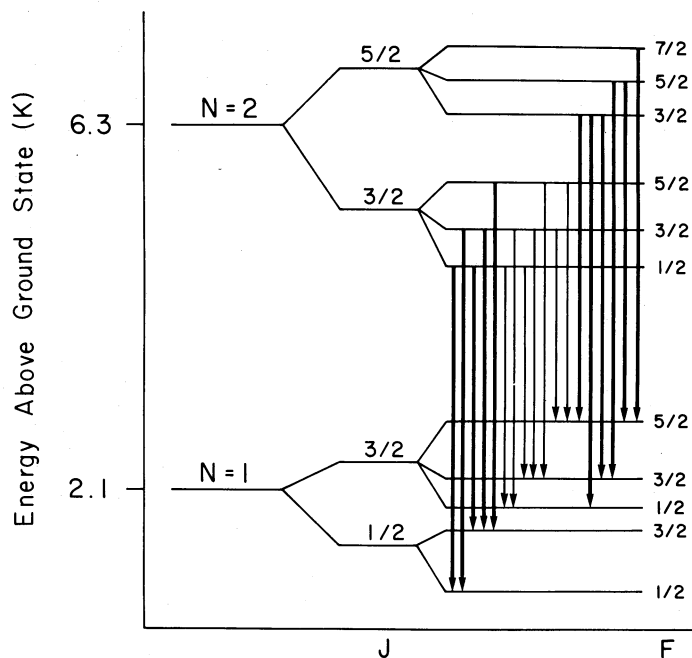


FIG. 1.—Energy level diagram for $N = 2$ and $N = 1$ rotational levels of SiN ($^2\Sigma^+$). Spin-rotation splittings, J , and hyperfine splittings, F , are not drawn to scale. Arrows indicate electric-dipole transitions between the levels; heavier arrows show the transitions searched for in this work.

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TABLE 1
OBSERVATIONAL DATA FOR SiN AND SiO

SOURCE	α (1950.0)	δ (1950.0)	V_{LSR} (km s^{-1})	T_R (K)		
				SiN: $N = 2-1^a$ ($J = 5/2-3/2$)	SiN: $N = 2-1$ ($J = 3/2-1/2$)	SiO: $J = 2-1$
Orion-KL	05 ^h 32 ^m 46 ^s .8	-05°24'13".0	+8.9	<0.026	...	3.5 (0.20)
IRC +10216	09 45 14.8	+13 30 40.0	-26	<0.018	<0.025	0.55 (0.042)
Sgr B2	17 44 11.0	-28 22 30.0	+62	<0.037	...	1.7 (0.11)
DR 21(OH)	20 37 14.5	+42 12 00.0	-5	<0.023	...	1.1 ^b (0.3)

^a Upper limits are 3σ in 1 MHz filters at FCRAO, except DR 21(OH), where 1.2 MHz filters were used at Hat Creek. Uncertainties for SiO line temperatures are 1σ .

^b Data from Downes *et al.* 1982, beam size = $43''$.

II. EQUIPMENT AND OBSERVATIONS

The Hat Creek observations at 87.5 GHz were performed between 1982 August 25 and September 2. The receiver was a cooled Schottky mixer, used in conjunction with two 25-channel filter banks of 1.2 MHz-wide channels and one 64-channel filter bank with 250 kHz filters. The mixer response to the upper and lower sidebands was assumed equal. The average system temperature was 350–400 K (single-sideband [SSB]), and the half-power beamwidth of the telescope was 2.3. The aperture efficiency, $\eta_A = 0.35$, was obtained from observations of Venus and Mars. The beam efficiency, measured by observing the Moon, was 0.54. Observing was done in position-switching mode, and pointing, estimated to be accurate to 0.5, was checked twice daily on Venus and Jupiter. The temperature scale was established by the chopper-wheel method (Penzias and Burrus 1973). Intensities are estimated to be accurate to 30%.

Observations at FCRAO utilized the cooled 80–120 GHz receiver and quasi-optical sideband filter with the image sideband terminated at 15 K. Two 256-channel filter banks of 1 MHz- and 250 kHz-wide channels were the spectrometers employed. The observations were performed during 1983 March and April, and at the observing frequencies the typical SSB system temperatures were 350–400 K including radome and sky corrections. The temperature scale was established using the chopper-wheel method and is accurate to 20%. The data were taken by position-switching in azimuth.

Venus was used as the calibration and pointing source for Orion-KL and Sgr B2 observations of SiN. Because of the

large declination of IRC +10216, spectral-line pointing on this source for the SiN observations was performed at the frequency of ^{12}CO , and the receiver was then returned to SiN. The frequency independence of the pointing was established during antenna tests earlier in the year. For the SiO observations, pointing on Orion-KL was done on Venus, pointing on Sgr B2 on Jupiter, and pointing on IRC +10216 on itself. The pointing is believed to be accurate to $15''$. Continuum scans in azimuth and elevation across Venus (brightness temperature at 87 GHz assumed to be 363 K: Good and Schloerb 1983; Ulich *et al.* 1980) gave a beam size of $61''$ and a main beam efficiency, η_B , of 0.56 at both SiN and SiO frequencies.

III. DATA

The data are presented in Tables 1 and 2 and Figures 2 and 3. In Table 1 we list the source positions and velocities, the observed 3σ limits to the SiN radiation temperatures (defined as the chopper-wheel-calibrated antenna temperature divided by the main beam efficiency, i.e., $T_R = T_A^*/\eta_B$), and the observed radiation temperatures of SiO: $J = 2-1$, $v = 0$. The radiation temperatures and line widths of the other lines appearing in the passbands of the SiN spectra are listed in Table 2.

Figure 2 shows the spectra obtained toward Sgr B2 and Orion-KL. The predicted SiN hyperfine patterns are shown beneath each spectrum. The strong lines to the right in each spectrum correspond to the $N = 1-0$, $(J, F) = (1/2, 1)-(1/2, 0)$ transition of CCH at 87.446 GHz (Lovas, Snyder, and Johnson 1979); the CCH transition shows significant blueshifted

TABLE 2
OBSERVATIONAL DATA FOR OTHER LINES IN PASSBAND

SPECIES	REF.	TRANSITION	FREQUENCY (MHz)	ORION-KL		IRC +10216		SGR B2		DR 21(OH)	
				T_R (K) ^a (ΔT)	$\Delta V_{1/2}$ ^b	T_R (K) ^a (ΔT)	$\Delta V_{1/2}$ ^b	T_R (K) ^a (ΔT)	$\Delta V_{1/2}$ ^b	T_R (K) ^a (ΔT)	$\Delta V_{1/2}$ ^b
^{30}SiS	1	$J = 5-4$	87550.6	<0.026	...	0.027 (0.006)	30	<0.037	...	<0.023	...
CCH	2	$N = 1-0$ $(J, F) = (1/2, 1)-(1/2, 0)$	87446	0.14 (0.0087)	11	0.063 (0.006)	31	0.13 (0.012)	18 ^c
HNCO	3	$J_{k-1, k+1} = 4_{14}-3_{13}$	87597	0.15 (0.0087)	12	<0.018	...	0.13 (0.012)	23
H	4	65 δ	87615.0	0.045 (0.0087)	29	<0.018	...	<0.037

^a All data taken with 1 MHz filters, except DR 21(OH), where 1.2 MHz filters were used. All upper limits are 3σ . Uncertainties for detections are 1σ .

^b Full width at half-maximum, in km s^{-1} .

^c Emission line affected by absorption. Width indicated is for emission feature only.

REFERENCES.—(1) Poynter and Pickett 1980. (2) Lovas, Snyder, and Johnson 1979. (3) Johansson *et al.* 1983. (4) Lilley and Palmer 1968.

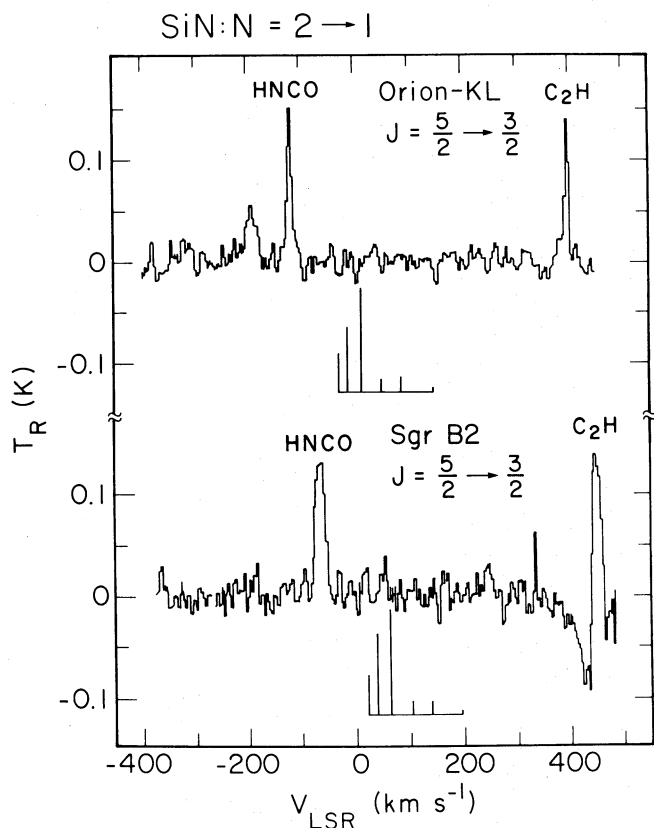


FIG. 2.—Spectra obtained toward Orion-KL and Sgr B2. The predicted hyperfine patterns of the $N = 2-1$, $J = 5/2-3/2$ multiplet of SiN are indicated. The strong lines toward the right of center are the $N = 1-0$, $(J, F) = (1/2, 1)-(1/2, 0)$ transition of CCH; those to the left are due to HNC O ($J_{k-1, k+1} = 4_{1,4}-3_{1,3}$). The feature to the far left in the Orion spectrum is possibly an H65 δ line.

absorption toward Sgr B2. The strong lines toward the left of center in each spectrum are due to the $J_{k-1, k+1} = 4_{1,4}-3_{1,3}$ transition of HNC O at 87.597 GHz (Johansson *et al.* 1983). There is a possibility of an H65 δ line at 87.615 GHz toward Orion-KL. We find no conclusive evidence for lines due to SiN. Similarly, no SiN was found toward DR 21(OH).

Figure 3 shows the spectra obtained toward IRC +10216. In this source we also looked for the $J = 3/2-1/2$ multiplet as well as the $J = 5/2-3/2$ set, and the appropriate hyperfine pattern is indicated. In addition to the 87.446 GHz C₂H line, the $J = 5/2-3/2$ spectrum shows a feature at approximately the frequency of the main hyperfine component of SiN: 87.55074 \pm 0.0015 GHz versus 87.5598 GHz (Saito, Endo, and Hirota 1983). The rejected sideband was observed to rule out the possibility of a strong line leaking through the filter. Also observations at different center frequencies enabled independent determination of the proper sideband for this line.

Identification of this line as arising from SiN fails for several reasons. Observations of several different molecules toward IRC +10216 (Olofsson *et al.* 1982) consistently show LSR velocities at -26 km s^{-1} , while this line, if due to SiN, would have to appear near $+5 \text{ km s}^{-1}$. Additionally, SiN has a strong hyperfine component [the $(J, F) = (5/2, 5/2)-(3/2, 3/2)$ transition] at 87.5675 GHz, which should blend with the main line in IRC +10216, leading to a line width *greater* than the 30 km s^{-1} typical of single transitions in this source (Olofsson *et al.* 1982). However, the measured width of the observed line is

30 km s^{-1} . Further evidence against identification as SiN is the lack of any features due to the $J = 3/2-1/2$ multiplet at 87.0 GHz for this molecule. This multiplet contains a hyperfine component which has 63% of the intensity of the main one at 87.5 GHz and should be apparent in the observed spectrum, unless non-LTE effects are occurring.

The $J = 5-4$ transition of ^{30}SiS , however, is at 87.5506 GHz (Poynter and Pickett 1980), and we identify the line in Figure 3 with this previously undetected species of silicon sulfide. The $J = 5$ level lies only 13 K above the ground state and should be excited in the circumstellar shell of IRC +10216. Furthermore, the observed radiation temperature is consistent with expected ratios of $^{29}\text{Si}/^{30}\text{Si}$ and $^{28}\text{Si}/^{30}\text{Si}$ when combined with observations of the more abundant isotopic species of SiS performed at Onsala (Olofsson *et al.* 1982; Johansson *et al.* 1983). Olofsson *et al.* (1982) were able to partially resolve the $J = 5-4$ emission from ^{28}SiS toward IRC +10216, although the ^{30}SiS line in Figure 3 shows the roughly square-topped emission profile characteristic of an unresolved optically thin expanding shell. Using the Onsala data and scaling our radiation temperature by the relative Onsala and FCRAO beam sizes, we derive the following silicon isotope ratios: $^{28}\text{Si}/^{30}\text{Si} = 31$ and $^{29}\text{Si}/^{30}\text{Si} = 1.3$ versus 29.8 and 1.5, respectively, for terrestrial ratios (Clark and Lovas 1977). As silicon isotopes are formed by explosive nucleosynthesis, terrestrial abundances are to be expected (Penzias 1981), provided chemical fractionation is negligible, and there are no masing effects in the SiS lines.

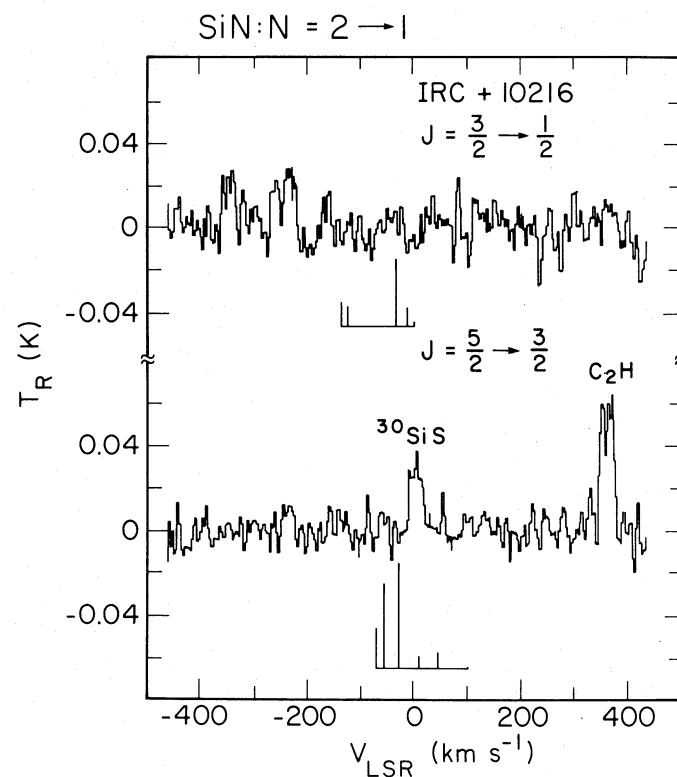


FIG. 3.—Spectra obtained toward IRC +10216 at the frequencies of both $N = 2-1$, $J = 5/2-3/2$ and $J = 3/2-1/2$ multiplets of SiN. Predicted hyperfine patterns are shown under each spectrum. The line near the main hyperfine component of the SiN $J = 5/2-3/2$ set we identify as the $J = 5-4$ transition of ^{30}SiS . The line at the right of center in the $J = 5/2-3/2$ spectrum is the $N = 1-0$, $(J, F) = (1/2, 1)-(1/2, 0)$ transition of CCH.

IV. DISCUSSION

A proper evaluation of the impact of these data on our understanding of silicon chemistry can be established through comparing (1) the abundance of SiN versus CN and (2) the abundance of SiN versus SiO. Unfortunately, the distributions of CN and thermal SiO are not the same in the sources observed. CN in the $N = 1-0$ transition appears to be extended over several arc minutes toward molecular clouds near H II regions such as Orion-KL, Sgr B2, and DR 21(OH) (Turner and Thaddeus 1977; Churchwell 1980). The angular extent of CN $N = 2-1$ emission toward IRC +10216 is some $73''$ (Wootten *et al.* 1982). SiO seems to be confined to regions of small angular extent ($\theta_s < 30''$) toward warm molecular clouds (Downes *et al.* 1982), and toward IRC +10216 (Olofsson *et al.* 1982). This confinement is most strikingly observed toward Orion-KL, where interferometer maps indicate that virtually all thermal SiO emission originates from an area of less than $10''$ for emission from the line center (Wright *et al.* 1983). Since the excitation requirements of CN and SiO are similar, the differences in their spatial extents must reflect chemical differences.

a) Column Densities

Table 3 presents estimates of the column densities for SiN and SiO based on Tables 1 and 2 and CN column densities from the literature. The column densities for SiN were derived using our calculated value of the dipole moment of SiN, 2.3 ± 0.2 debyes (Appendix), and assuming the $N = 2-1$ transition to be optically thin, the hyperfine components to have their LTE intensities, and the rotational partition function to be characterized by the kinetic temperatures, T_K , found for these sources (see Table 3). SiO column densities were calculated using the same rotational (= kinetic) temperatures as for SiN, and assuming the SiO emission to be optically thin, except for Orion-KL. In Table 3, where two values are given for the column density of SiN for a source, the first SiN column depth

was derived using the CN line width (zero power, from values in the literature), and the second assuming a line width identical to that observed for SiO. The 3σ noise level for T_R used for each source was averaged over the appropriate number of channels for a given expected line width to zero power.

Densities greater than $4 \times 10^5 \text{ cm}^{-3}$ are required to thermalize the SiN $N = 2$ level, and although we may be sampling such dense regions in our beam, it is more likely that SiN is subthermally excited. Provided $T_{\text{rot}} > 6.3 \text{ K}$, using $T_{\text{rot}} = T_K$ overestimates the total column densities; if $2.7 < T_{\text{rot}} < 6.3$, the total column densities are underestimated by at most a factor of 1.7. Thus, using $T_{\text{rot}} = T_K$ gives a reasonable estimate of the upper limits to the SiN column density. However, in IRC +10216, rotational excitation of molecules possessing large dipole moments probably occurs via radiative decay from IR-pumped vibrational levels, rather than from collisions, and the subsequent decay will tend to make $T_{\text{rot}} > T_K$ (Morris 1975; Morris and Alcock 1977; Olofsson *et al.* 1982): hence, for this source we are definitely overestimating the column density of SiN. In Orion-KL, interferometer observations (Wright *et al.* 1983) and silicon isotope ratios (Penzias 1981; Wolff 1980) indicate that the $J = 2-1$ SiO line is optically thick. Use of $\tau \sim 2$, a source kinetic temperature of 230 K, and a source size of $6'' \times 11''$ explains our observed SiO spectrum toward Orion-KL as well as the results mentioned above. For Orion-KL, then, a high temperature and small source size are appropriate for a SiN-SiO comparison, while a filled aperture and small line width are more appropriate for SiN-CN; hence, two different kinetic temperatures are indicated in Table 3.

b) SiN/CN Ratio

If SiN has a spatial distribution similar to CN, then comparison of the column densities to determine the abundance ratio should be direct. The sources observed in this work are extended with respect to both our beams and those used to measure CN emission (NRAO-Kitt Peak, Owens Valley Radio

TABLE 3
COMPARISON OF COLUMN DENSITIES AND UPPER LIMITS FOR SiN, CN, AND SiO

SOURCE	T_K^a	SiN ^b		CN		SiO			$\frac{\text{SiN}}{\text{CN}}$	$\frac{\text{SiN}}{\text{SiO}}$
		NL($N = 2$) ($\times 10^{12}$)	NL(tot) ($\times 10^{14}$)	ΔV_{zp}^c (km s^{-1})	NL(tot) ($\times 10^{14}$)	ΔV_{zp}^c (km s^{-1})	NL($J = 2$) ($\times 10^{12}$)	NL(tot) ($\times 10^{14}$)		
Orion-KL	70 ^d	<0.45	<0.066	8 ^e	$\geq 2.5,^e 6.1^f$	<0.011-0.026	...
	230 ^g	<58 ^h	<26 ^h	40	5000 ^h	2260 ^h	...	<0.012
IRC + 10216	16 ⁱ	<0.61	<0.027	30 ⁱ	17 ⁱ	30	7.2	0.33	<0.0016	<0.082
Sgr B2 ^j	20 ^k	<1.03	<0.054	20 ^f	3.4 ^f	20	8.0	0.42	<0.016	<0.13
DR 21(OH)	30 ^d	<0.44	<0.031	8 ^e	$\geq 0.37,^e 0.94^l$	<0.033-0.084	...
		<0.71	<0.050	20 ^m	4.0	0.28	...	<0.18 ($<1.8^n$)

^a Assumed kinetic temperature.

^b Derived from the $(J, F) = (5/2, 7/2) - (3/2, 5/2)$ transition, assuming τ small and LTE. $\text{NL}(N = 2) = 3k(2N + 1) \int T_R dV / 8\pi^3(N)\mu_o^2 v_{\text{HF}} = 3.37 \times 10^{12} \int T_R dV$ (cm^{-2}), where f_{HF} is the hyperfine component relative intensity, and μ_o is the permanent dipole moment; V is in km s^{-1} .

^c Approximate zero power line widths. SiN column density derived using observed CN or SiO width.

^d Linke and Goldsmith 1980.

^e Churchwell 1980.

^f Allen and Knapp 1978.

^g Wright *et al.* 1983.

^h Source size correction applied; assumed size was $6'' \times 11''$ and $\tau(^{28}\text{SiO}) \sim 2$.

ⁱ Wootten *et al.* 1982.

^j 52 km s^{-1} component only.

^k Scoville, Solomon, and Penzias 1975.

^l Turner and Gammon 1975.

^m Downes *et al.* 1982.

ⁿ Corrected for ratio of Onsala to Hat Creek beam sizes.

Observatory). The SiN/CN ratios are indicated in Table 3. If SiN is formed by simple ion-molecule chemistry, Turner and Dalgarno (1977) suggest that the abundance of this molecule reflects that of CN, scaled by the silicon-to-carbon ratio, i.e., $\text{SiN/CN} \sim \text{Si/C} \sim 0.1$. Our observations indicate that SiN/CN is significantly less than 0.1. Their predictions, however, are only qualitative and apply to less dense regions than we have probably observed. Additionally, most ion-molecule reaction rates for silicon species are not known (Turner and Dalgarno 1977; Millar 1980). Since the abundance of CN can be explained by gas phase ion-molecule chemistry (Watson and Walmsley 1982), one can conclude that either such chemistry does not favorably synthesize SiN, or that silicon is depleted because of grain formation in gas where CN is present. Atomic silicon is depleted by at least a factor of 10 relative to its cosmic abundance toward diffuse clouds (Morton 1974), and Knapp, Kuiper, and Brown (1976) have measured a depletion factor of 15 for silicon in the dark cloud ρ Oph.

In the circumstellar shell of IRC +10216, however, ion-molecule chemistry is probably not important for molecular synthesis (Zuckerman 1980, and references therein). Instead, thermodynamic chemical equilibrium prevails in the inner shell, and molecular abundances may be "frozen" throughout the outer shell regions, except near the shell edge, where photodestruction dominates (McCabe, Connon Smith, and Clegg 1979; Lafont, Lucas, and Omont 1982). Radicals such as CN may be primarily formed by photodestruction of frozen parent species, for example, HCN (Wootten *et al.* 1982). A likely source of SiN is photodestruction of the parent molecules HSiN and HNSi, but, as is often found for silicon analogs of carbon-containing molecules, HSiN is not as stable as HCN and is likely to have a very low abundance. If the freezing model is correct, it could explain the low abundance of SiN in this source relative to CN. The presence of SiO and SiS in IRC +10216 indicates that not all silicon is depleted onto grains and some must remain for molecule formation.

c) SiN/SiO Ratio

Conversely, if SiN is formed primarily in regions where SiO is abundant, then both the molecules come from sources which are unresolved in most millimeter-wave telescope beams, and source coupling factors become critical. We measured SiO $J = 2-1$ spectra with the FCRAO antenna to compare with SiN for all sources except DR 21(OH), where Onsala data (Downes *et al.* 1982) were used. The SiO transition is very close in frequency to the $N = 2-1$ SiN transitions; hence the beam sizes were identical for measurements made with the same telescope. If very similar reaction pathways produce and destroy both molecules, then SiN/SiO might reflect the N/O ratio. Table 3 lists the SiN/SiO ratios, as well as the SiO column densities derived from the FCRAO observations. For Orion-KL and IRC +10216, the derived ratios differ significantly from the N/O ratio of 0.13 (York *et al.* 1983).

The large column density of SiO present in Orion-KL indicates that a considerable amount of silicon *must* be present in the gas phase. The low ratio of SiN relative to SiO may be a result of an overabundance of oxygen toward Orion-KL or a depletion of nitrogen. Chemical calculations by Prasad and Huntress (1982) suggest that a rich oxygen environment is needed to explain the high abundance of SO relative to CS in the Orion "plateau" feature. However, recent Hat Creek interferometer maps show that SO and SiO may not be present in the same gas toward this source (Plambeck *et al.* 1982; Wright *et al.* 1983). If nitrogen is being chemically channeled into other

molecules, such as ammonia, little may be available for SiN formation. Such an enhancement in NH_3 is probably occurring in Orion-KL (Watson 1982), though the detailed distribution of the ammonia gas may differ from the SiO gas (Genzel *et al.* 1982; Pauls *et al.* 1983).

Shocks could cause the detailed chemical synthesis of SiN to differ from that of SiO. The large column depth of SiO toward Orion-KL has been postulated to be the result of shock chemistry (Lada, Oppenheimer, and Hartquist 1978). In this scheme the shock enhancement of OH followed by the endothermic reaction of $\text{Si} + \text{OH} \rightarrow \text{SiO} + \text{H}$ enriches the SiO column density behind a shock front. Just such an increase in OH is observed toward Orion-KL (Watson 1982). However, such shock enhancement may also be applicable to SiN. Calculations by Mitchell and Deavau (1982) and Prasad and Hollenbach (1980) have shown that the abundance increase behind a shock front for NH is expected to be similar to that for OH. The reaction $\text{Si} + \text{NH} \rightarrow \text{SiN} + \text{H}$ is thermodynamically favorable (JANAF Thermochemical Tables). The activation energy of this reaction is not known but is probably unimportant for hot shocked gas. Frequencies for NH have been measured with sufficient accuracy to allow astronomical searches for this possible SiN precursor, but lie in the far-infrared.

Millar (1980) suggests that SiO is formed on grain surfaces, but accurate laboratory data are lacking. Grain growth may occur via SiO_2 mantle formation (Harris, Woolf, and Rieke 1978; Whittet and Blades 1980), and it may be the destruction of such mantles in the Orion-KL outflow which produces an atypically large abundance of SiO. Also SiS has not been conclusively detected toward Orion-KL (see Dickinson and Rodriguez Kuiper 1981).

V. SUMMARY

We have searched for the $N = 2-1$ transition at 87 GHz of a possible new interstellar silicon species, SiN. SiN was not seen to a very low level (column density $< 10^{12}-10^{15} \text{ cm}^{-2}$) toward sources where both SiO and CN are abundant and SiS is observed. We report detection of a new species of silicon sulfide, ^{30}SiS , at $87.55074 \pm 0.0015 \text{ GHz}$ ($J = 5-4$).

Comparison of the upper limits to the abundance of SiN versus measured abundances of CN shows that the SiN/CN ratios are significantly less than 0.1, the cosmic Si/C ratio; these data suggest that silicon may be depleted onto grains relative to carbon, or that chemical pathways producing CN, most likely gas-phase ion-molecule reactions, do not synthesize much SiN.

Toward IRC +10216 and Orion-KL, the derived upper limits for the SiN abundance relative to SiO do appreciably deviate from the cosmic N/O ratio. SiN appears depleted with respect to SiO, indicating that the N/O ratio has little impact on silicon chemistry. Shock chemistry in Orion-KL may be responsible for the SiO enhancement relative to SiN, but destruction of SiO-type grain mantles in the Orion-KL outflow may be a more favored explanation. Alternatively, oxygen may be overabundant in this source, favoring SiO production, or nitrogen may be locked up in other molecules and not available for SiN formation.

In IRC +10216, SiN may be formed via photodestruction of the parent molecules HNSi and HSiN, which we believe to have low abundances in this source for chemical stability reasons. Accurate laboratory frequencies and radio-frequency searches for these molecules will aid our understanding of why interstellar and circumstellar space seems "SiN-free."

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APPENDIX

AB INITIO CALCULATION OF THE DIPOLE MOMENT OF SILICON NITRIDE

The theoretical calculation of the silicon nitride dipole moment was carried out at both the self-consistent-field (SCF) and single and double excitation configuration interaction (CISD) levels of theory using both double zeta plus polarization (DZ + *P*) and triple zeta plus polarization (TZ + *P*) basis sets. In the CI treatment, the core self-consistent-field molecular orbitals (essentially 1s, 2s, 2p, Si; 1s, N) were held doubly occupied in all configurations. Similarly, the four σ and one π core counterparts in the virtual space were deleted from the CI. The actual CI calculations were performed in the subgroup C_{2v} , in which there were 3714 configurations for the DZ + *P* CI and 7067 configurations for the TZ + *P* CI. For both levels of theory, analytic energy first derivative methods were used to optimize the bond length.

The DZ + *P* basis is a standard Dunning-Hay (1977)

(11s7p1d/6s4p1d), $\alpha_d = 0.6$ basis on silicon and the analogous Huzinaga (1965)–Dunning (1970), $\alpha_d = 0.8$ basis for nitrogen. This yielded a SCF bond length of 1.535 Å and a CISD bond length of 1.566 Å (cf. 1.5721 Å from experimental work of Saito, Endo, and Hirota 1983). The SCF and CISD dipole moments are, respectively, 2.48 and 2.34 debyes (with polarity Si⁺N⁻).

In order to check for any gross basis set dependence, the calculations were repeated with the DZ + *P* basis “uncontracted” to nearly TZ + *P*: on silicon (11s7p1d/8s5p1d), $\alpha_d = 0.6$ and on nitrogen (9s5p1d/5s3p1d), $\alpha_d = 0.8$. Using this basis, the CISD calculation yielded an equilibrium bond length of 1.565 Å and a dipole moment of 2.3 debyes, in good agreement with DZ + *P* results. We suggest error bars of ± 0.2 debyes for the prediction $\mu(\text{SiN}) = 2.3$ debyes.

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