1988ApJ...329L.113N

THE ASTROPHYSICAL JOURNAL, 329:L113–L116, 1988 June 15

SiH AND THE UNIDENTIFIED 4.6 MICRON FEATURE

JOSEPH A. NUTH
NASA/Goddard Space Flight Center
AND
MARLA H. MOORE
Chemistry Department, University of Maryland
Received 1987 December 14; accepted 1988 March 22

ABSTRACT

Results from experimental studies of the irradiation of SiH_4-H_2O and $Fe(CO)_5$-SiH_4-H_2O ice mixtures at 15 K using 1 MeV protons have revealed the synthesis of a very stable infrared spectral feature at 4.6 μm which is characteristic of the SiH functional group. This feature persists through warmup of the ice, exposure to air at 300 K, and vacuum annealing to at least 400 K. Because of the high cosmic abundance of both silicon and hydrogen and the unexpected stability of the SiH feature in our experiments, we suggest that SiH might be responsible for the 4.6 μm absorption feature observed in W33A.

Subject headings: interstellar: grains — interstellar: molecules — laboratory spectra

I. INTRODUCTION

An absorption feature at 4.6 μm was first observed by Soifer *et al.* (1979) in W33A and was attributed by them to CO absorbed on grains. The feature has been reobserved in W33A on several occasions (Lacy *et al.* 1984; Geballe *et al.* 1985; Larson *et al.* 1985), and in two of these papers the feature has been attributed to a different species. Following Soifer *et al.* (1979), Lacy *et al.* (1984) used higher resolution observations ($\lambda/\Delta\lambda \approx 840$) and demonstrated the presence of three components within the 4.6 μm band. They attributed two of these features to CO: a sharp feature at 2140 cm^{-1} due to solid CO and a broad wing at 2135 cm^{-1} due to CO complexed with "other molecules." The third component at 2165 cm^{-1} was attributed to one or more molecules containing CN bonds; this component was dubbed "XCN." Larson *et al.* (1985) observed W33A with a resolution ($\lambda/\Delta\lambda$) of ~2000 in search of additional structure within the 4.6 μm bands. None was detected. Because of the position of the absorption, they identified the feature at 4.62 μm (2165 cm^{-1}) as due to methyl isocyanide (CH_3NC). More recently, Grim and Greenberg (1987) have assigned the 4.62 μm absorption feature to OCN^- ions trapped in ice mantles on the surfaces of grains, based on a comprehensive study of the spectral features which appear in irradiated ices composed of varying chemical and isotopic fractions of C, H, O, and N.

We report here the results of a laboratory study of the irradiation of a very different ice mixture, one composed of varying fractions of Si, H, C, O, and Fe. Studies of this nature were suggested to us several years ago by A. G. G. M. Tielens (private communication) based on the (then) recently calculated and very high grain destruction rates in interstellar shocks (Seab and Shull 1985). The reasoning was that once a large fraction of silicate grains were atomized, recondensation of this material would occur slowly on the few surviving grain cores. As metal atoms accreted on the surfaces of these cores, recombination with surface adsorbed hydrogen atoms appeared to be more likely than did the recrystallization of a silicate. This might produce various silanes (Si_nH_{2n+2}) or metal hydrides. As grains continued to cool behind the shock, molecules such as H_2O, CH_4, or CO which may have formed either in the gas or on grain surfaces would accrete along with the remaining metal atoms. Would the processing of this ice mantle, containing refractory atomic or molecular species, produce 10 and 20 μm "silicate" features upon irradiation by cosmic rays or UV photons? If irradiation of these mixtures could not reproduce these features, then either the calculated grain destruction rates were too high or an unknown and efficient mechanism existed which assured the production of material whose infrared spectra was similar to that of silicate grains observed in oxygen-rich circumstellar shells.

We will report the detailed results of our experiments in a later paper. We will concentrate in this *Letter* on only one aspect of our studies, the discovery that the synthesized SiH feature at 4.6 μm is much more stable than we would have expected (especially in the presence of oxygen) and that SiH on grain surfaces could be responsible for the observed 4.6 μm feature in W33A. We note that an SiH functional group bound to amorphous silicate grains might in many ways be analogous to CH functional groups bound to small carbon particles—e.g., hydrogenated amorphous carbon (HAC) grains—which have been proposed as a likely component of the grain population in interstellar clouds (Duley and Williams 1981, 1983). Our experiments will be described in § II, and our results will be presented in § III. In § IV we will discuss the implications of our results for W33A and for the general interstellar grain population. Our conclusions are contained in § V.

II. EXPERIMENTAL PROCEDURE

The results of experiments on two ice mixtures, $Fe(CO)_5$-SiH_4-H_2O and SiH_4-H_2O will be reported here: the experimental apparatus has been previously described by Moore (1984). In both cases we first made up an appropriate gas mixture in a 5 liter bulb consisting of 12 torr H_2O, 4 torr $Fe(CO)_5$, and 4 torr SiH_4 or 12 torr H_2O and 8 torr SiH_4, respectively. This mixture was slowly deposited onto a polished aluminum substrate mounted on the cold finger of a cryostat at 15 K until a layer of ice approximately 7 μm thick was formed: the infrared spectrum of this ice mixture was recorded. The sample was then irradiated with 1 MeV protons, after which the spectrum of the ice was again recorded. Two additional cycles of irradiation/spectroscopy were carried out. The three doses of protons provided a cumulative incident flux of 3×10^{14}, 7×10^{14} and 1×10^{15} protons cm^{-2}, respectively.

After irradiation at 15 K to a cumulative dose of 10^{15} protons cm^{-2}, the samples were warmed to 50 K and thereafter in 50 K steps up to 300 K. After each warmup an infrared spectrum of the ice or residue was recorded. Samples warmed to 300 K were left under vacuum for 72 hr and then removed for further analysis. In both cases an infrared spectrum of the residue was obtained in air at room temperature using a Perkin-Elmer grating spectrometer. The residue from the $Fe(CO)_5$-SiH_4-H_2O irradiation and warmup was annealed in vacuo for 30 hr at 400 K and the infrared spectrum of this sample was again recorded.

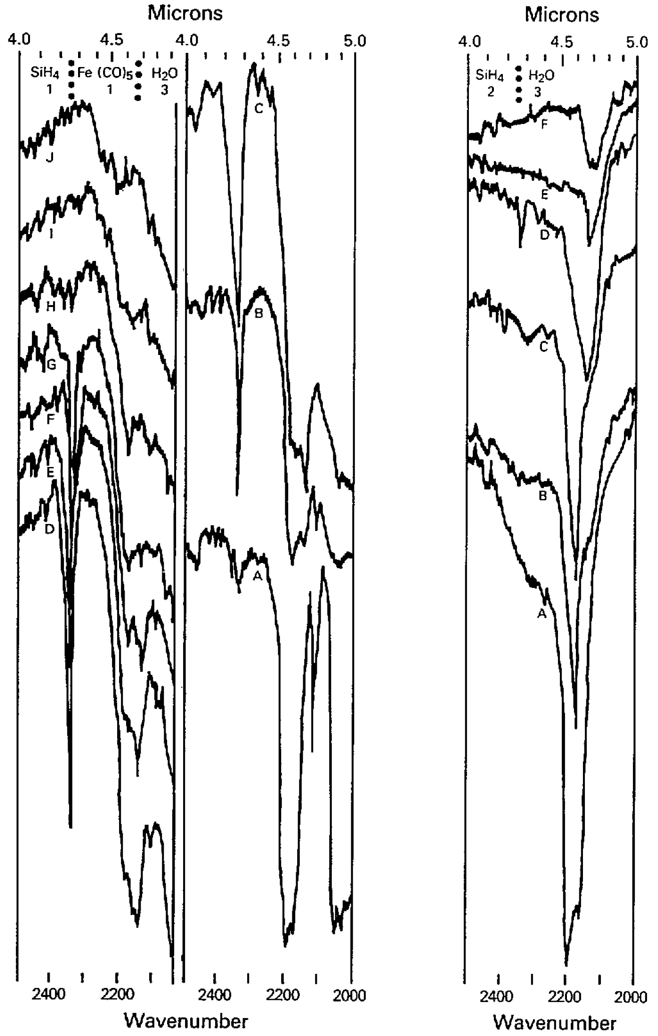

FIG. 1.—Infrared spectra of $Fe(CO)_5$-SiH_4-H_2O (1 : 1 : 3) (*left*) and SiH_4-H_2O (2 : 3) ices (*right*) over the wavelength range between 4 and 5 μm as a function of radiation dose and annealing. For the $Fe(CO)_5$-SiH_4-H_2O mixture, curve A is the spectrum of the original mixture at 15 K, curve B is after 1 MeV irradiation to 3×10^{14} protons cm^{-2}; curve C after a dose of 7×10^{14} protons cm^{-2}; and curve D after a dose of 10^{15} protons cm^{-2}. Curve E is the spectrum after warmup to 50 K, while curves F–J represent spectra taken after warmup to 100 K, 150 K, 200 K, 250 K, and 300 K, respectively. For the SiH_4-H_2O (2 : 3) mixtures, curves A–D represent the same conditions as for the $Fe(CO)_5$-SiH_4-H_2O (1 : 1 : 3) mixture above. Curves E and F are spectra taken after the sample was warmed to 150 K and 200 K, respectively.

III. RESULTS

The infrared absorption spectra of the $Fe(CO)_5$-SiH_4-H_2O and SiH_4-H_2O samples between 4 and 5 μm are shown in Figure 1. For the SiH_4-H_2O experiment we show the spectrum of the original deposit (A), the spectrum after each of three irradiation steps (B–D), and after warmup to 150 K and to 200 K. For the $Fe(CO)_5$-SiH_4-H_2O experiment we show the spectrum of the original deposit (A), that after the three irradiation steps (B–D), and after warmup to 50 K (E), 100 K (F), 150 K (G), 200 K (H), 250 K (I), and 300 K (J). For the convenience of the reader, we have included a table of the central positions of the peaks and shoulders within the 4.6 μm band for both experimental runs (Table 1). Note that in Figure 1 the broad absorption near 2000 cm^{-1} is due to the CO stretch of the $Fe(CO)_5$, while the sharp peak at 2342 cm^{-1} is due to CO_2 made during the irradiation. These features are not tabulated. Figure 2 is the infrared spectrum of the $Fe(CO)_5$-SiH_4-H_2O residue after warmup to 300 K for 72 hr (*bottom*) and to 400 K for 30 hr (*top*) in vacuo over the spectral range from 2.5 to 50 μm. It is obvious from the intensity of the 4.6 μm feature that an appreciable concentration of silicon hydride is formed during irradiation along with the silicate which is responsible for the 10 and 20 μm features. The features at 3 and 6 μm are due to water (of hydration). The feature at $\sim$2050 cm^{-1} in the bottom curve is due to the CO stretch from $Fe(CO)_5$ trapped within the residue. To check the possibility that the residue resulted from chemical reactions within the warming ice, a similar gas mixture was condensed and warmed without proton irradiation. The infrared spectrum of the substrate, after warming to room temperature, revealed no residue.

IV. DISCUSSION

Our experiments are not meant to be direct simulations of the radiative processing of realistic grain mantle mixtures containing various metallic hydrides and molecular ices. Our experiments are intended to be the first in a series of increasingly complex studies which lead toward this goal. These first studies were a test to see if further experiments were warranted, e.g., if the 10 and 20 μm silicate features were not observed in experiments on such concentrated metal hydride ices or if a strong absorption feature were detected in the processed ices which was not detected in interstellar spectra, then there would be some doubt about the utility of further experiments. Since this was not the case, we plan to irradiate a series of more complex mixtures containing metals plus such molecular ices as CO, CO_2, CH_4, and NH_3. We plan to study the products from such mixtures after UV photolysis as well as after irradiation by 1 MeV protons.

In Figure 1, for the simple SiH_4-H_2O mixture, the evolution of the SiH absorption band (peaks at 2200 cm^{-1} and 2165 cm^{-1}) is fairly straightforward: a small amount of irradiation eliminates the 2200 cm^{-1} component, while continued irradiation and warmup shifts the centroid of the absorption monotonically to longer wavelengths. Irradiation of the more complex mixture of $Fe(CO)_5$-SiH_4-H_2O does not behave as simply. As this mixture is irradiated, much more structure appears within the 4.6 μm band. This trend continues through both the irradiation and the warmup phases of the experiment. Although the initial shift of the band is toward longer wavelength, as the sample is warmed through about 150 K the band begins to shift back to shorter wavelength. Indeed, the peak absorption of the SiH feature in the residue (Fig. 2) occurs at a wavelength of 4.5 μm (2250 cm^{-1}).

TABLE 1

CENTRAL POSITIONS OF PEAKS AND SHOULDERS IN 4.6 MICRON BAND

Parameter	Original	Dose 1	Dose 2	Dose 3	50 K	100 K	150 K	200 K	250 K	300 K	300 K in air	400 K in air
						SiH_4-H_2O (2:3) Ice						
Curve	A	B	C	D	...	...	E	F	...	...	...	...
Value (cm^{-1})	2200	2175	2170	2170	...	...	2140	2140	...	...	2230	...
Value (μm)	4.55	4.60	4.61	4.61	...	...	4.67	4.67	...	...	4.48	...
Value (cm^{-1})	2165	...	...	2140	...	...	...	2120	...	...	2180	...
Value (μm)	4.62	...	...	4.67	...	...	...	4.71	...	...	4.59	...
						$Fe(CO)_5$-SiH_4-H_2O (1:1:3) Ice						
Curve	A	B	C	D	E	F	G	H	I	J	...	...
Value (cm^{-1})	2190	2180	2180	2180	2170	2170	2170	2170	2190	2240	2280	2230
Value (μm)	4.57	4.59	4.59	4.59	4.61	4.61	4.61	4.61	4.57	4.46	4.39	4.48
Value (cm^{-1})	2170	2140	2150	2160	2140	2135	2135	2150	2155	2200	2230	...
Value (μm)	4.61	4.67	4.65	4.63	4.67	4.68	4.68	4.65	4.64	4.55	4.48	...
Value (cm^{-1})	...	...	...	2140	...	...	2100	2110	2115	2170	2190	...
Value (μm)	...	...	...	4.67	...	...	4.76	4.74	4.73	4.61	4.57	...

Although it is probable that judicious combinations of the various processed spectra shown in Figure 1 could conceivably be matched with an arbitrary degree of precision to the observed spectrum of W33A over the 4–5 μm interval, we do not feel that such an exercise would be worthwhile at this time. If W33A is indeed a protostar (Lacy *et al.* 1984), then the grains and grain mantles within this region have been through many stages of processing. It seems quite possible that all stages of processing may be represented in such a cloud, from fully formed icy mantles to thoroughly processed organic and refractory shells. Too few constraints exist at this time to make a meaningful spectral "match" between observations and experiment. However, several points can still be made based on our experiments.

First, there is little doubt that some grains are destroyed in interstellar shocks (Seab and Shull 1985) and that the free metal atoms eventually do recondense somewhere. Given the abundance of hydrogen, it seems likely that at least some silicon atoms will form SiH bonds. It may also be possible to form such bonds when amorphous silicates, previously formed in circumstellar environments, are exposed to hydrogen atoms in the interstellar medium, but experimental studies would be needed to confirm this hypothesis. No matter what the primary formation mechanism is, because of the relatively high cosmic abundance of both Si and H, and because the SiH bond is stable, it is reasonable to expect to detect the SiH vibrational fundamental in a silicate grain mantle in much the same manner as one might expect to detect the CH vibrational fun-

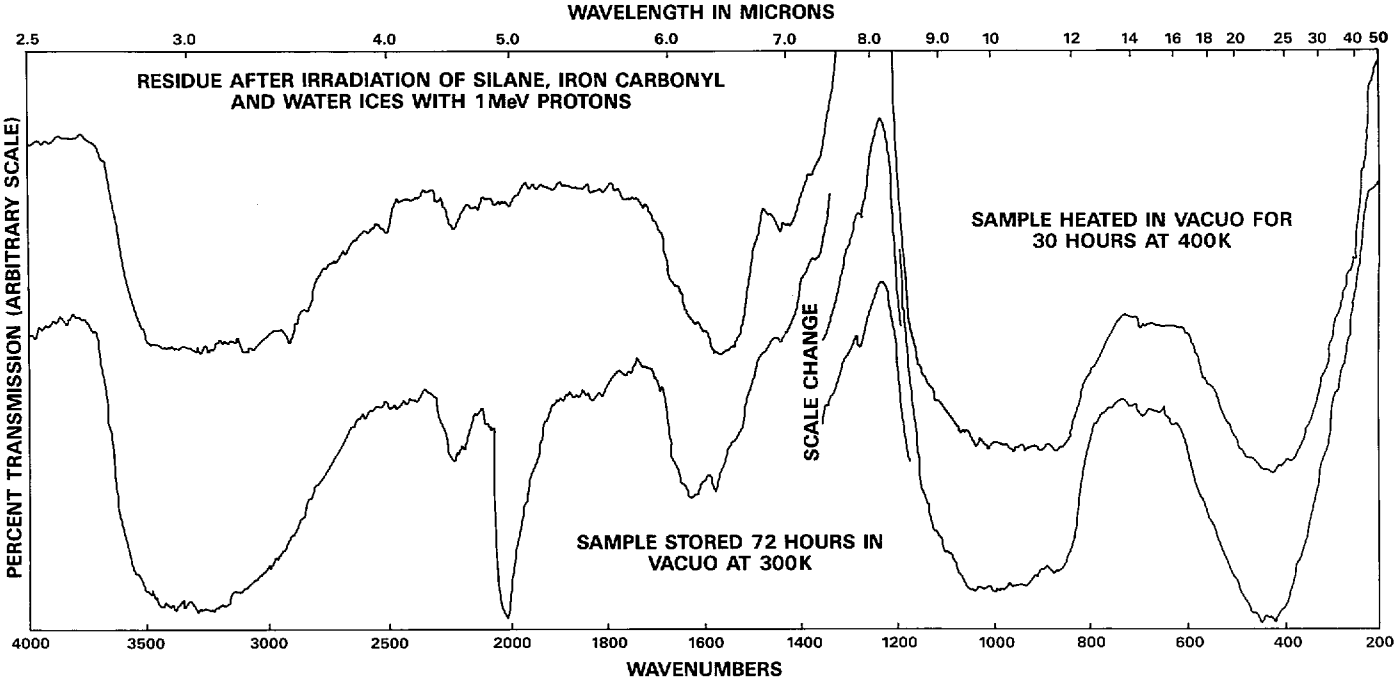

FIG. 2.—Infrared spectra between 2.5 and 50 μm of the $Fe(CO)_5$-SiH_4-H_2O (1:1:3) ice residue after irradiation by 1 MeV protons to a total dose of 10^{15} protons cm^{-1} and warmup under vacuum to 300 K for 72 hr (*bottom curve*) and after vacuum annealing at 400 K for 30 hr (*top curve*).

damental in a carbonaceous grain. If W33A does indeed contain some highly processed grains, then SiH could be responsible for the 4.6 μm feature.

A second point which can be made based on our experimental data is the remarkable stability of the SiH bond. Since silane is volatile and extremely flammable in air, it was quite a surprise to see the persistence of the 4.6 μm feature, not only after annealing in vacuo at 300 K for 72 hr, but also after having been exposed to air twice (for the IR spectroscopy) and after vacuum annealing at 400 K for 30 hr. The feature could not have been due to silane trapped or adsorbed at sites either within or on the surface of the residue since silane is not stable in air at room temperature. The SiH must have been covalently bonded into the silicate network. It should be remembered that silicon is similar to carbon in its ability to covalently bond up to four other atoms simultaneously, so that it is possible for silicon to be bound into a silicate network and still have the ability to bind one, two, or even three hydrogen atoms.

We can use our data for the absorbance of the SiO stretch at 10 μm to estimate a value for the integrated absorbance of the SiH feature at 4.6 μm provided that we assume that, at most, only one SiH bond exists for each amorphous $FeSiO_3$ "molecule" in our sample. Day (1981) measured the peak mass absorption coefficient for amorphous $FeSiO_3$ as 2100 cm^2 g^{-1}. His sample shows a full width at half-maximum of $\sim$200 cm^{-1}. $FeSiO_3$ has a molecular weight of 132 g $mole^{-1}$; thus the 10 μm SiO stretch for $FeSiO_3$ has an integrated absorbance of $\sim 9.2 \times 10^{-17}$ cm $molecule^{-1}$. Comparison of the integrated intensity in the 4.6 μm feature to that in the 10 μm SiO stretch in spectra of our samples obtained at 150 K and 250 K yield integrated absorbance values of 3.4×10^{-17} and 7.0×10^{-17} cm $molecule^{-1}$, respectively, for the strength of the SiH stretch assuming one SiH for each $FeSiO_3$. This is obviously the minimum possible value for this quantity since it is more likely that only a small fraction of the silicon remains bonded to hydrogen in these samples. Based on our measurements, an integrated absorption strength of more than 10^{-16} cm $molecule^{-1}$ does not seem to be unreasonable.

Taniguchi *et al.* (1980) give a value for the peak absorbance at $\sim$2050 cm^{-1} of a hydrogenated amorphous silicon film of $\sim$1000 cm^{-1}. The FWHM of this feature is $\sim$150 cm^{-1}. If we assume an average molecular weight of 29 for the film, so that there is one H atom per silicon atom (an upper limit) and that the average density of the film is $\sim$2 g cm^{-3}, we calculate an integrated absorbance of $\sim 4 \times 10^{-18}$ cm $molecule^{-1}$. Knights (1979) gives a value for the peak absorbance of SiH in amorphous silicon deposited at 373 K of $\sim$1600 cm^{-1} which decreases with increasing temperature. This decrease is due to the decrease in the amount of H incorporated into the lattice at higher temperatures. Typical hydrogen concentrations for such films are a few percent on an atomic basis (Hirose 1986). If we assume that there are roughly 25 silicon atoms for every hydrogen atom, then the data of Taniguchi *et al.* (1980) and of Knights (1979) yield an integrated absorbance of 10^{-16} cm $molecule^{-1}$ for an individual SiH bond which is consistent with our previous estimate based on the relative strength of this feature in our residue.

Using the minimum absorbance strength from our experiments (3.4×10^{-17}) and the data of Grim and Greenberg (1987) for the strength of the absorption toward W33A, we require a column density of "SiH" of $\sim 1.1 \times 10^{18}$ cm^{-2} to explain the observations. This would require that $\sim$10% of the available silicon be associated with at least one hydrogen atom: this value appears high, even when one considers that, because each silicon atom is capable of forming four chemical bonds, only one bond in 40 would have to be a hydrogen atom. If the absorption strength of SiH is on the order of 10^{-16} cm $molecule^{-1}$, however, only one silicon bond in a thousand would be to hydrogen. This would seem to be much more reasonable.

Finally, we suggest that ice-metal mixtures deserve more consideration in both models and experiments relating to the chemistry of interstellar grain mantles.

V. CONCLUSION

The infrared spectra of residues of proton-irradiated SiH_4-H_2O and $Fe(CO)_5$-SiH_4-H_2O icy mixtures reveal a remarkably stable feature near 4.6 μm which we attribute to the SiH functional group. The peak of the SiH absorption varies between about 4.46 and 4.74 μm, depending upon the composition of the matrix and the degree of irradiation and annealing of the samples. Based on the high cosmic abundance of both silicon and hydrogen, the relative strength of the 4.6 μm feature in our samples compared to the strength of the 10 and 20 μm silicate absorptions, the unexpected stability of the SiH bond, and the fact that grains in W33A are likely to be highly processed, we suggest that the 4.6 μm feature observed in W33A might be due to SiH bound either into or on the surfaces of amorphous silicate grains.

REFERENCES

Day, K. L. 1981, *Ap. J.*, **246**, 110.

Duley, W. W., and Williams, D. A. 1981, *M.N.R.A.S.*, **196**, 269.

———. 1983, *M.N.R.A.S.*, **205**, 67P.

Geballe, T. R., Baas, F., Greenberg, J. M., and Schutte, W. 1985, *Astr. Ap.*, **146**, L6.

Grim, R. J. A., and Greenberg, J. M. 1987, *Ap. J. (Letters)*, **321**, L91.

Hirose, M. 1986, in *Plasma Deposited Thin Films*, ed. J. Mort and F. Jansen (Boca Raton, FL: CRC Press), p. 24.

Knights, J. C. 1979, *Japanese J. Appl. Phys.*, Vol. **18**, Suppl. 1, p. 101.

Lacy, J. H., Baas, F., Allamandola, L. J., Persson, S. E., McGregor, P. J., Lonsdale, C. J., Geballe, T. R., and van de Bult, C. E. P. 1984, *Ap. J.*, **276**, 533.

Larson, H. P., Davis, D. S., Black, J. H., and Fink, U. 1985, *Ap. J.*, **299**, 873.

Moore, M. H. 1984, *Icarus*, **59**, 114.

Seab, C. G., and Shull, J. M. 1985, in *Interrelationships Among Circumstellar, Interstellar, and Interplanetary Dust*, ed. J. A. Nuth and R. E. Stencel (NASA CP-2403; Washington: GPO), p. 37.

Soifer, B. T., Puetter, R. C., Russell, R. W., Willner, S. P., Harvey, P. M., and Gillett, F. C. 1979, *Ap. J. (Letters)*, **232**, L53.

Taniguchi, M., Hirose, M., Hamasaki, T., and Osaka, Y. 1980, *Appl. Phys. Letters*, **37**, 787.

Marla H. Moore: Chemistry Department, University of Maryland, College Park, MD 20742

Joseph A. Nuth: NASA/Goddard Space Flight Center, Code 691, Greenbelt, MD 20771