Infrared Spectra of Silicon Difluoride in Neon and Argon Matrices

J. W. Hastie, R. H. Hauge, and J. L. Margrave

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received November 25, 1968*

Abstract: The species SiF_2, produced by the reduction of SiF_4 over Si metal at 1150°, has been isolated in solid neon and argon. From infrared absorption spectra the symmetric and antisymmetric fundamental frequencies have been obtained for the various natural isotopic species of SiF_2. Also from these measurements the bond angle of SiF_2 was calculated and found to be in good agreement with the known gas-phase value, thus indicating the absence of appreciable matrix effects. Absorptions attributable to polymeric SiF_2 were also observed.

A previous study[1] of SiF_2, matrix-isolated in solid argon, did not give conclusive evidence for the fundamental frequencies of this species. Also, a subsequent gas-phase study[2] indicated that the region of the fundamental symmetric and antisymmetric stretches overlapped strongly and neither frequency was well defined. As the matrix isolation technique allows optimum resolution, under these circumstances a reexamination of the SiF_2 ir spectrum by this method seemed desirable. Also, the gas-phase geometry of SiF_2 is well established from microwave spectra[3] and thus provides an opportunity to check the accuracy and reliability of the isotope shift method in matrices for the determination of bond angles of difluoride species. It is of considerable interest to determine whether the gas-phase geometry of a molecule can be obtained using a rare gas matrix environment particularly as the isotope shift method in matrices is now being used to determine geometries for high-temperature reactive species which are not conveniently studied by other methods.[4] Similar studies have been made for other molecules of known geometry such as SO_2 and SeO_2.[5] The availability of three naturally occurring Si isotopes allows the isotope shift method to be utilized in this case.

Table I. Infrared Spectra for SiF_2 Species in Neon and Argon Matrices

Ne matrix frequency, cm^{-1}	Assignment[a]	Ar matrix frequency, cm^{-1} (±0.1)
838.0_3	$*\nu_1$-$Si^{30}F_2$	. . .
841.0_5	ν_1-$Si^{30}F_2$	832.0
843.1_4	$*\nu_1$-$Si^{29}F_2$	. . .
845.6	ν_1-$Si^{29}F_2$	837.5
847.0_3	$*\nu_3$-$Si^{30}F_2$	. . .
849.7_8	$*\nu_1$-$Si^{28}F_2$	. . .
851.0_1	ν_1-$Si^{28}F_2$	842.8
851.3 (sh)	ν_3-$Si^{30}F_2$	840.1
855.1_4	$*\nu_3$-$Si^{29}F_2$	. . .
856.8_1	P_3	. . .
858.1_1	ν_3-$Si^{29}F_2$	846.1[c] (sh)
859.6	P_2	. . .
861.5_8	$*\nu_3$-$Si^{28}F_2$	. . .
862.7_2	P_1	. . .
864.6[b]	ν_3-$Si^{28}F_2$	852.9[b]

[a] An asterisk indicates matrix split peaks; P_1, P_2, and P_3 are polymer peaks. [b] All frequencies were measured relative to these values which have an absolute uncertainty of ±0.1 cm^{-1}, using the rotational bands of H_2O for calibration (ref 6). However, the dispersion of the instrument is accurately known and suitably sharp relative frequencies, or frequency differences, are reproducible to ±0.05 cm^{-1}. [c] The true position of this peak is affected by the considerable overlap with the more intense adjacent adsorptions.

Experimental and Results

Infrared spectra were recorded with a Beckman IR-9 spectrophotometer over the spectral range of 400–2000 cm^{-1}. Frequency calibration, for the regions of observed spectra, was conveniently made using the standard atmospheric H_2O spectrum.[6] Absolute frequency values could be reproducibly measured to ±0.1 cm^{-1} and frequency differences to ±0.05 cm^{-1} for well-defined peaks. No noticeable change in frequency calibration over frequency intervals of 50 cm^{-1} was found.

The technique for preparation of gaseous SiF_2 from solid Si and gaseous SiF_4 is well established,[1,2] and the matrix trapping apparatus and procedure have also been described elsewhere.[7] The SiF_2 and unreacted SiF_4 gas were allowed to pass through a ~30-cm length of 0.25-in. Cu tubing (room temperature) before cocondensation with the rare gas on a gold-plated mirror at near liquid He temperatures. Relative flow rates of SiF_4 and rare gas were adjusted to give theoretical rare gas to SiF_2 molar ratios of between several hundred and a thousand.

Observed infrared spectra for SiF_2 and related species, isolated in argon and neon matrices, are given in Figures 1 and 2, respectively. Conditions corresponding to a resolution of 0.8 cm^{-1} were used.

Spectrum A of Figure 1 represents the most dilute of the various matrices studied and differs appreciably from the previously reported spectrum[1] in an argon matrix where probably poor isolation conditions existed. The higher

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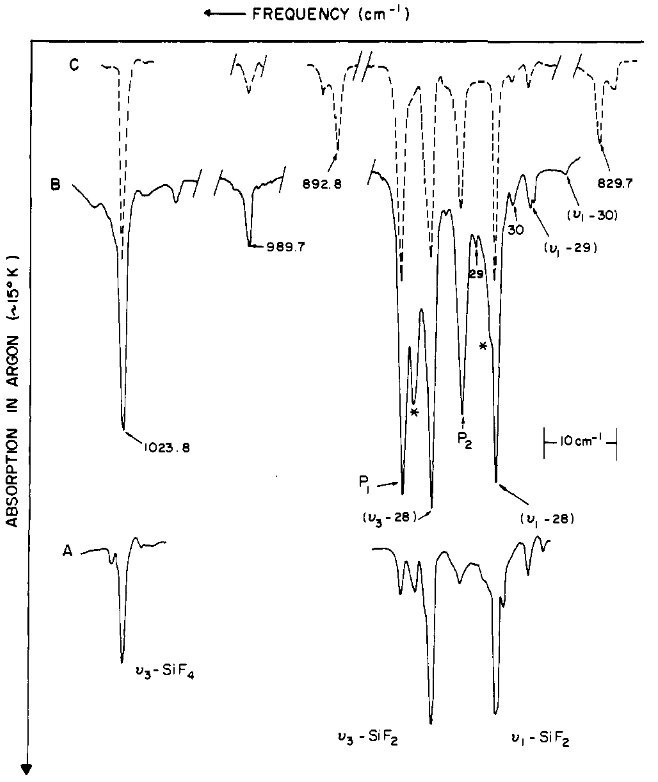

Figure 1. Infrared spectra of silicon fluoride species produced by reaction of SiF_4 with Si metal at 1150° and cocondensation of the volatile[4] products (room temperature) with argon at ~15°K to form a dilute matrix. Spectrum A resulted from a relatively high rare gas to product concentration. Spectrum B represents a rare gas to product concentration lower by a factor of ~5 than for spectrum A. Spectrum C is the result of a warm-up of spectrum B to ~42°K for several minutes and recooling to the original matrix temperature. The indicated frequencies are uncalibrated and are high by 0.5 cm^{-1}.

concentration matrix indicated as spectrum B of Figure 1 shows the growth of several of the initially weak bands. If the two strongest bands of spectrum A, Figure 1, are assigned to the ν_1 and ν_3 stretches of SiF_2, then the other comparatively intense features of spectra B and C must either be the result of molecular association in the matrix, *e.g.*, the dimer $(SiF_2)_2$, or a matrix splitting of the monomeric frequencies. Matrix splitting can often be removed by warming and recooling of the matrix while polymeric species tend to increase. Thus the features of spectrum B, indicated by an asterisk, are most likely matrix split peaks, and those denoted as P_1 and P_2 are most likely due to polymeric species. The bands indicated as (ν_3-28, 29, and 30) are taken to be the ν_3 frequencies for the $Si^{28}F_2$, $Si^{29}F_2$, and $Si^{30}F_2$ species. The relative intensities are of the correct order of magnitude. Similarly, the ν_1 isotopic bands are indicated. The following discussion of the more intense neon matrix spectra will verify that this is an unambiguous assignment. Other features in the spectra are the result of either gas-phase or matrix reactions of SiF_2 with itself or with SiF_4. The ν_2 frequency for SiF_2 is known to fall below the 400-cm^{-1} limit of the spectrometer used for this study.

The neon matrix spectra, shown in Figure 2, were obtained from relatively high matrix concentrations to emphasize the low abundance isotopic features. The bands marked by an asterisk may in this case be definitely attributed to matrix splitting as they can be removed by annealing the matrix. The isotopic features are reproducible and have the correct relative abundance. For more dilute matrices the absorptions denoted by P_1, P_2, and P_3 were absent and are therefore very likely due to polymeric species. Frequency measurements and assignments for these bands and those for the argon matrix spectra are summarized in Table I.

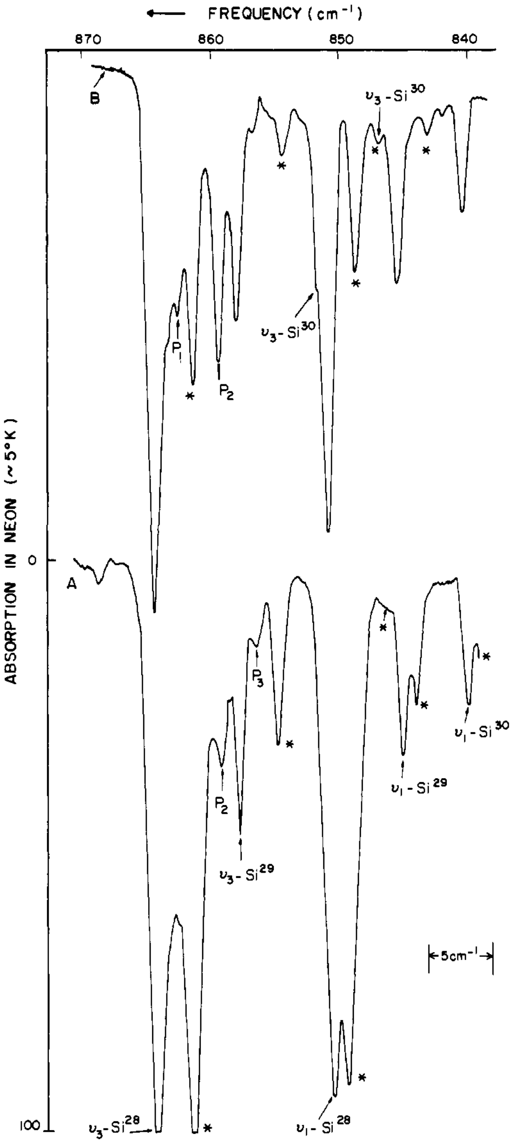

Figure 2. Infrared spectra of silicon fluoride species isolated in a neon matrix and showing the region of the ν_3 and ν_1 frequencies for SiF_2. Spectrum A was obtained by trapping at ~5°K, and spectrum B is the result of an annealing warm-up and recooling of spectrum A.

From these isotopic frequency measurements, for the ν_3 stretch as assigned, and treating ν_3 as ω_3 of a gas-phase molecule as outlined previously,[5] the following bond angles are calculated. For the neon matrix an angle of $97.5 \pm 1°$ is indicated, and this value is essentially constant for both sets of matrix split frequencies. An error of ± 0.1 cm^{-1} in the frequency separation would lead to an uncertainty of only $\pm 1.6°$ in the calculated bond angle. In argon where the frequency measurements are less well defined because of overlapping absorptions, an average value of 102 ± 2° is measured. From analogy with similar species, and with SiF where $\omega_e x_e = 6.2\ \text{cm}^{-1}$, the anharmonic correction to the frequency values can be assumed to be of the order of 5–10 cm^{-1}, and one finds the anharmonic correction to have only a small effect on the bond angle in this case. For example, using an anharmonic factor of 8 cm^{-1}, the neon matrix angle increases to 100.5 ± 1°, as compared to the gas-phase value of 100.9°. Thus it can be concluded that within the limits of experimental uncertainty the calculated geometry of matrix-isolated SiF_2 is essentially the same as that in the gas phase.

A verification of the ν_3 and ν_1 assignments is given by the fact that if the ν_1 isotopic frequencies were assumed to be ν_3, a bond angle calculation would indicate values of only 81 ± 2°. This differs too much from the gas-phase value for this alternative assignment to be correct. The assignment verifies the current literature[2] where the higher frequency is taken to be the ν_3. The following comparison of frequencies for ν_3 of 872 cm^{-1} in the gas phase, 864.6 cm^{-1} in the neon matrix at ~5°K, and 852.9 cm^{-1} in the argon matrix at ~15°K and similarly for ν_1 of 855, 851.5, and 842.8 cm^{-1} indicates that neon matrices give SiF_2 stretching frequencies that are only slightly shifted to the red from the gas-phase values. This has also been found to be the case for other inorganic species such as SO_2, SeO_2, SiO, and GeF_2.[5,7] Also the sharpness of the bands, as shown in Figure 2, indicates another advantage of using neon as compared with other rare gases for the matrix in this type of spectroscopy.

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Stereochemistry of Polynuclear Compounds of the Main Group Elements. VII.[1] The Structure of Octamethyldialuminummonomagnesium[2]

J. L. Atwood and G. D. Stucky

Contribution from the Department of Chemistry and Chemical Engineering and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.

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Abstract: Dimethylmagnesium dissolves in trimethylaluminum to give two crystalline compounds with melting points of 39 and 54°. The crystal structure of the lower melting electron-deficient product octamethyldialuminummonomagnesium, $Mg[Al(CH_3)_4]_2$, has been determined by three-dimensional, single-crystal X-ray diffraction techniques. The compound crystallizes in the triclinic space group $P\bar{1}$, with two molecules per unit cell. The cell parameters are $a = 6.955$, $b = 10.802$, and $c = 10.287$ Å and $\alpha = 102.35$, $\beta = 105.03$, and $\gamma = 92.49°$. The average magnesium–carbon(bridge)–aluminum angle is 77.7°, and the average magnesium–aluminum distance, 2.704 Å. The conventional discrepancy index for the structure is 7.2%. Nuclear magnetic resonance studies on the trimethylaluminum–dimethylmagnesium and trimethylaluminum–dimethylberyllium systems are reported. In the latter, low-temperature spectra are interpreted in terms of the formation of a complex with the empirical formula $Be[Al(CH_3)_4]_2$.

The heterocyclic four-membered ring systems formed by group II and III metals with two one-electron alkyl and aryl donors are unusual in having metal–metal distances approximately equal to their single bond metallic diameters, and relatively small metal–carbon–metal bridge angles ranging from 66 to 78°.[3] These features together with bond lengths, the observed phenyl ring distortions in triphenylaluminum,[4] and the terminal carbon–aluminum–terminal carbon angle of 123.1° in trimethylaluminum[5] have been used as the basis for speculation concerning the bonding in group II and III electron-deficient compounds.

In order to learn more about the relative stereochemical importance of (1) metal–metal interactions, (2) steric effects of groups external to the heterocyclic ring, (3) steric effects across the ring between bridging atoms, (4) dative ligand–metal π bonding, (5) the electron distribution about the bridging atom in isoelectronic series of the type R_3C–, R_2N–, RO–, and F^-, and (6) intermolecular forces within the crystal lattice, we have initiated a systematic investigation of a number of polynuclear systems. In addition, it is hoped that such a study will provide realistic models for the extensive synthetic chemistry involving group II and III organometallic complexes as intermediates. In this paper the structural features of $(CH_3)_8MgAl_2$, and the nuclear magnetic resonance spectra of $(CH_3)_2Mg$–$Al(CH_3)_3$ and $(CH_3)_2Be$–$Al(CH_3)_3$ systems are discussed.

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