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Argon Matrix Investigation of the 1:1 Molecular Complexes of Silicon Tetrafluoride with Water, Methanol, and Dimethyl Ether

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Abstract: The codeposition of SiF_4 with a variety of oxygen-containing bases in inert matrices at 15 K has given rise to a number of novel 1:1 adducts. The species $H_2O{\cdot}SiF_4$, $CH_3OH{\cdot}SiF_4$, and $(CH_3)_2O{\cdot}SiF_4$ were each identified and characterized spectroscopically. The most prominent feature in the infrared spectrum of each adduct was an intense Si–F stretching mode between 960 and 990 cm^{-1}. The position of this mode correlated linearly with the degree of base character of the Lewis base in the complex. Additional modes of the 1:1 complex were observed as well, including modes of the perturbed base subunit in the adduct. These modes showed little shift from the position of the free, isolated base, indicating a quite weak, but specific, interaction with SiF_4. No evidence of a 1:2 adduct was noted under these experimental conditions.

Introduction

The acid/base chemistry and complexing ability of SiF_4 has continued to be of interest to chemists in a variety of fields.[1-3] Many adducts of SiF_4 are known with nitrogen-containing bases,[4-6] the majority of which are 1:2 adducts. Recently, the matrix isolation technique was employed to investigate the intermediate 1:1 adducts,[7] such as $SiF_4{\cdot}NH_3$. The structure of this adduct was determined to be trigonal bipyramidal about the central silicon, with the amine ligand in an axial position. Further matrix studies supported this structural conclusion,[8] as have recent ab initio calculations.[9] During this work, a preliminary investigation was made into the complex formation of SiF_4 and $(CH_3)_2O$, and no reaction was observed.

Little is known about complexes of SiF_4 with oxygen-containing bases, presumably owing to the much weaker interaction. A few 1:2 adducts[10] have been reported at temperatures substantially below room temperature, including the complex $SiF_4{\cdot}2(CH_3)_2O$. The heat of formation of this latter complex from the gas-phase reactants was reported to be −9.0 kcal/mol, compared to roughly −54 kcal/mol for the $SiF_4{\cdot}2NH_3$ complex.[11] On the other hand, it is reported that the reaction of SiF_4 with H_2O does not lead to adduct formation,[12] but rather hydrolysis ultimately to SiO_2 and HF, although one group has tentatively reported[13] the formation of a 1:2 adduct $SiF_4{\cdot}2H_2O$. In contrast to these observations, the reaction of SiF_4 with CH_3OH reportedly forms a 1:4 complex,[14] with the four methanol units hydrogen bonded to the fluorines on SiF_4. Margrave and co-workers[15] have studied the interaction of SiF_2 and SiF_4 with CH_3OH, and report that the reaction of SiF_4 with CH_3OH leads to formation of CH_3OSiF_3 + HF. However, these experiments were conducted at elevated temperatures (before condensation at −196 °C) and equilibration of the gases was allowed to occur.

The diversity of these results suggests a thorough reinvestigation using the matrix isolation technique. In addition, previous experiments in this laboratory in which SiF_4 was deposited into argon matrices have shown one weak, unexplained product band at 984 cm^{-1}, which appeared to be sensitive to the level of impurity water in the particular experiment. Finally, if complexes of SiF_4 with oxygen-containing bases are stable, then spectral data from these complexes might be combined with the known results for the amine complexes to provide some correlation of spectral features with basicity of the donor molecule. With this background, a complete matrix isolation study of the complexes of SiF_4 with H_2O, CH_3OH, and $(CH_3)_2O$ was undertaken.

Experimental Section

The matrix isolation experiments performed in this study were carried out on apparatus which has been described previously.[16] The majority of the spectra were recorded on a Beckman IR 12 infrared spectrophotometer, over the region 4000–200 cm^{-1}. More recent spectra were recorded on a Perkin-Elmer 983 infrared spectrometer, employing an IR data station for spectral handling and storage. Resolution in either case was on the order of 1 cm^{-1} at 1000 cm^{-1}, and slightly greater in other spectral regions. H_2O (triply distilled), D_2O (Merck, 98%), CH_3OH (MCB, Spectrograde), and $(C_2H_5)_2O$ (Fisher) were introduced into the vacuum system via a glass finger and were subjected to several freeze–thaw cycles prior to sample deposition. $(CH_3)_2O$ (Matheson), $(CD_3)_2O$ (Merck, 98%), and SiF_4 (Matheson) were introduced into the vacuum system via lecture bottles and were also subjected to freeze–thaw cycles prior to sample preparation. Argon and nitrogen were used as matrix gases, and were generally used without further purification. However, on a few occasions the matrix gases were passed through a copper coil immersed in liquid nitrogen to remove traces of H_2O.

Samples were generally deposited from separate vacuum lines onto the 14 K cold window for 20–24 h before final scans were recorded. In a few experiments, samples were deposited from a concentric deposition device in an attempt to increase product yield. This technique will be discussed in more detail in a future publication.[17]

Results

Prior to the investigation of any of the reactions of interest, blank experiments were conducted with each reactant alone in either argon or nitrogen. It should be noted that all of these blank experiments contained a low level of H_2O, primarily from degassing of the stainless steel walls of the vacuum vessel. This did not present any complications other than in blank experiments of SiF_4 in either Ar or N_2, as will be discussed below. Experiments in which either pure argon or pure nitrogen were deposited then served as "H_2O" blanks, and were run immediately after an SiF_4 blank. Blank experiments were conducted on CH_3OH, $(CH_3)_2O$, and $(C_2H_5)_2O$ at dilutions ranging from 200/1 to 2000/1, and spectra were in agreement with literature spectra in argon matrices, when available.[18,19]

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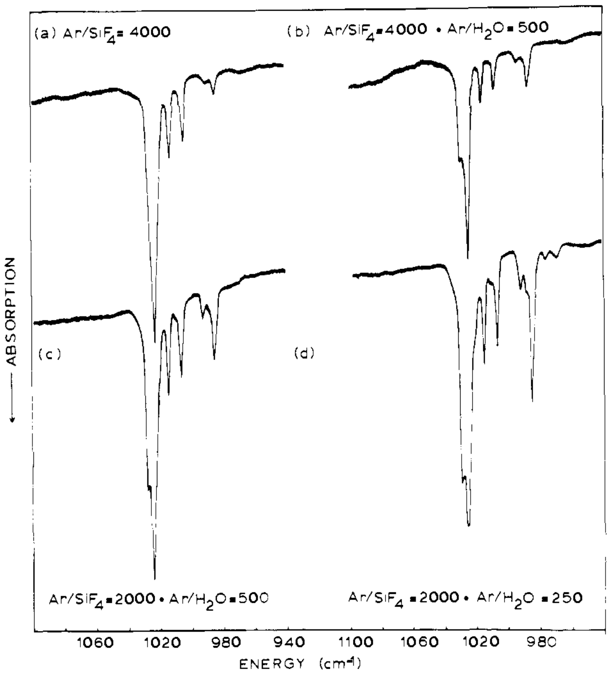

Figure 1. Infrared spectra, over the region 940–1100 cm^{-1}, of the reaction products of the codeposition of SiF_4 with H_2O into argon matrices. In trace a, H_2O is present at impurity levels only.

SiF_4 + H_2O. The matrix reaction of SiF_4 with H_2O was studied under a variety of conditions in both argon and nitrogen matrices. Since all matrices contain at least a trace of H_2O impurity, blank experiments of Ar/SiF_4 can serve as SiF_4 + H_2O codeposition experiments with very high dilutions. The infrared spectrum of a sample of Ar/SiF_4 = 4000 showed an intense feature at 1023 cm^{-1}, with lesser sharp features at 1013 and 1015 cm^{-1}. These latter two bands correspond to ^{29}Si and ^{30}Si components of the 1023-cm^{-1} band, as silicon occurs naturally as ^{28}Si, ^{29}Si, and ^{30}Si, in a 92:5:3 ratio.[20] In addition, a doublet was observed weakly at 991 and 984 cm^{-1}, with the 984-cm^{-1} band being the more intense of the two, but still considerably weaker than the 1005- and 1013-cm^{-1} bands. When a sample of Ar/SiF_4 = 4000 was codeposited with a sample of Ar/H_2O = 500, a similar spectrum was obtained, except that the doublet at 991 and 984 cm^{-1} grew in intensity relative to the parent SiF_4 bands, and now the 984-cm^{-1} component was of comparable intensity to the 1013-cm^{-1} parent band. Representative spectra of the products of SiF_4 + H_2O codeposition experiments in argon matrices are shown in Figure 1.

This type of experiment was repeated numerous times, sometimes with additional H_2O, and sometimes with just the impurity level present in all experiments. In all experiments, it was readily apparent that the intensity of the 984-cm^{-1} band was directly related to the level of H_2O in the sample, although it, of course, also grew as the concentration of SiF_4 was increased. In the most concentrated samples, an optical density of about 0.60 was obtained, and in these experiments two weaker bands were observed at 969 and 976 cm^{-1}, which can be attributed to ^{29}Si and ^{30}Si isotopic counterparts of the 984-cm^{-1} band. In addition, weak features were observed in the region and 400 cm^{-1}, near the SiF_4 parent deformation mode at 385 cm^{-1}.

One set of experiments was also conducted on a PE983 infrared spectrometer, with computer data handling capabilities. In these experiments, the region near the parent H_2O vibrations was monitored closely and compared with blank experiments run immediately before the reaction with SiF_4. H_2O is known[21-23] to rotate in argon matrices, as well as dimerize, giving rise to a relatively complex spectrum in the 3700- and 1600-cm^{-1} regions. It is also known that as a dopant is added to an argon matrix,[24] this rotational structure is partially inhibited, and a "rotationless" H_2O band grows in, at 1591 cm^{-1} for bending mode, and around 3730 cm^{-1} for the antisymmetric stretching mode. When a sample of Ar/SiF_4 = 200 was deposited, infrared spectra were recorded in the H_2O regions, and then a comparable blank experiment of argon with impurity H_2O was subtracted; the result is shown in Figure 2. Two features are observed in the 1600-cm^{-1} region, at 1591 and a closely spaced doublet at 1598 and 1600 cm^{-1}, the former being due to rotationless H_2O. In the upper region, computer subtraction showed a band at 3730 cm^{-1} due to rotationless H_2O in argon, and an additional product band at 3722 cm^{-1}.

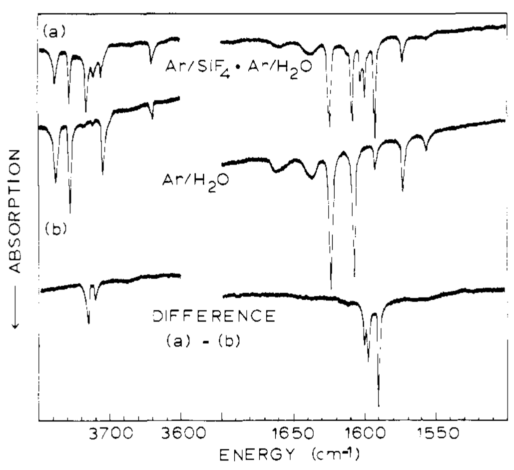

Figure 2. Infrared spectra, over the regions 1500–1700 and 3600–3800 cm^{-1}, of the reaction products of the codeposition of SiF_4 with H_2O in argon matrices. The bottom trace is the difference spectrum between the upper and middle traces, showing bands due to "rotationless" H_2O in argon, and the product bands.

Similar results were obtained when a nitrogen matrix was employed, although overall yields were decreased, as has been observed for a number of other systems. In addition, the observed product bands were somewhat broader in nitrogen. In the Si–F stretching region, a weak doublet was observed when SiF_4 was trapped in an N_2 matrix, at 988 and 981 cm^{-1}, in addition to the parent bands of SiF_4. When a sample of N_2/H_2O was codeposited with a sample of N_2/SiF_4, the doublet at 988 and 981 cm^{-1} grew in intensity relative to the SiF_4 parent bands, but never reached the level of absorption observed in argon matrices. Similar computer subtraction experiments were conducted in the H_2O regions; the spectra were generally less complicated, as rotational structure[25] is eliminated in N_2. One band was observed at 1604 cm^{-1} in the N_2/SiF_4 = 200 experiment, which was not present in an N_2 blank, while a possible product band was detected at 3672 cm^{-1} in the upper spectral region.

Two experiments were conducted using mixed Ar/N_2 matrices to determine whether formation of the apparent product bands was due to removal of degeneracy of the SiF_4 mode at 1023 cm^{-1} by impurities in the matrix. At ratios of Ar/N_2/SiF_4 = 2000/4/1 and 1600/400/1, no intensification of the 984 cm^{-1} band was observed, although both parent and product bands broadened somewhat in these experiments.

SiF_4 was also codeposited with D_2O in both argon and nitrogen matrices, at several dilute concentrations. In all experiments, the results were identical with those for H_2O; the bands at 984 and 991 cm^{-1} did not show a measurable shift, possibly 0.1 to 0.2 cm^{-1}, but resolution limts preclude on accurate statement. No product bands were observed in the parent D_2O spectral regions, which is not unexpected in that the rotational bands of D_2O are more

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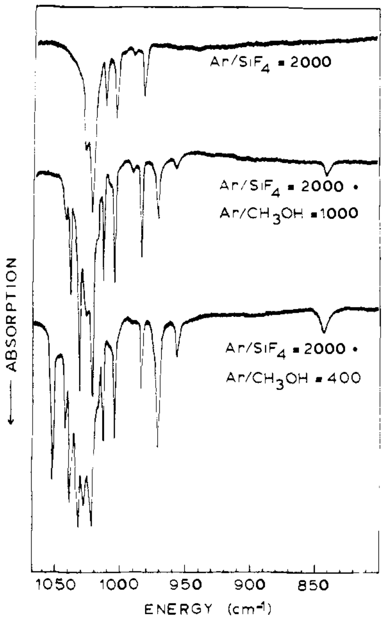

Figure 3. Infrared spectra of the reaction products of the codeposition of SiF_4 with CH_3OH in argon matrices, over a range of concentrations, in the Si–F stretching region.

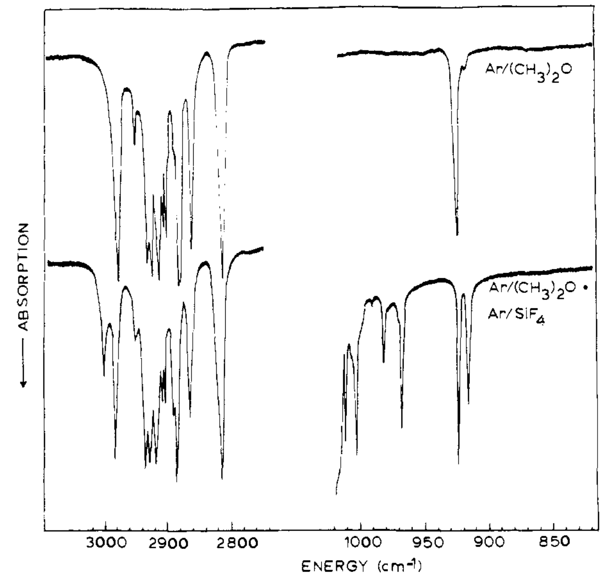

Figure 4. Infrared spectra, over the regions 810–1020 and 2700-3100 cm^{-1} of the reaction products of the codeposition of SiF_4 with $(CH_3)_2O$ in argon, compared with a comparable blank experiment of dimethyl ether in argon.

closely spaced than those of H_2O because of a smaller rotational constant, and observation of a weak product band, even with spectral subtraction, was not possible.

SiF_4 + CH_4OH. Methanol was codeposited with SiF_4 in argon matrices in a number of experiments, over a wide range of concentrations. When a sample of Ar/SiF_4 = 2000 was codeposited with a sample of Ar/CH_3OH = 1000, two product bands were observed, in addition to the 984, 991 doublet seen in the H_2O experiments and in all other experiments involving SiF_4. These two product bands were located at 972 and 957 cm^{-1}, with the 972-cm^{-1} band being the more intense of the two. As the concentrations were increased stepwise up to M/R = 250 for each reactant in the most concentrated experiments, these two product bands were observed to grow steadily, until the 972-cm^{-1} band was nearly full absorbing in the most concentrated experiment. Under these conditions, two new product band was observed, at 844 and 406 cm^{-1}, both of which were decidedly broader than the original two product bands. Careful inspection was made of the spectral regions where CH_3OH is known to absorb, and no new bands were observed which could be ascribed to a product species. The four product bands which were observed, at 972, 957, 844, and 406 cm^{-1}, did appear to maintain a constant relative intensity ratio over the range of concentrations used. Infrared spectra of the reaction products of the codeposition of SiF_4 with CH_3OH in argon at varying concentrations are shown in Figure 3.

SiF_4 + $(CH_3)_2O$. Dimethyl ether was codeposited with samples of SiF_4 in argon matrices over a large range of concentrations and deposition conditions, and several product bands were detected. The most intense band, as has been the pattern throughout, was a doublet at 969 and 962 cm^{-1}, with the 969-cm^{-1} band being the more intense. The intensity of this band ranged from an optical density of 0.10 when the total dilution was 1/1/4000 to fully absorbing with concentrations of 1/1/500. At these higher concentrations, several modes of the base molecule were observed as well, shifted only a few wavenumbers from the parent species. These bands, which were of reasonable intensity, but less than the 969-cm^{-1} band, were located at 917, 1078, 1180, and 3006 cm^{-1}; several of these product bands are presented in the traces of Figure 4. Presumably other vibrational modes of the perturbed dimethyl ether unit were not shifted sufficiently from the modes of the parent molecule and were hidden by the intense parent bands. Finally, in these experiments, one band was observed near the deformation mode of SiF_4, at 372 cm^{-1}.

In one experiment, SiF_4 and $(CH_3)_2O$ were codeposited with argon from a single deposition line, after equilibration of the gas-phase mixture, with a dilution ratio of Ar/SiF_4/$(CH_3)_2O$ = 1000/1/1. In this experiment, the above set of product bands was again observed, and no additional bands were detected as a result of this mode of deposition. Moreover, the yield of product, as indicated by the intensity of the product band at 969 cm^{-1}, was no greater than that observed in the twin jet experiments when comparable concentrations were employed.

When $(CD_3)_2O$ was codeposited with SiF_4 over a range of concentrations, similar results were obtained, although with a lesser overall yield. The most distinctive features were again in the Si–F stretching region, shifted 1–2 cm^{-1} to lower energies from the $(CH_3)_2O$ counterparts, and were located at 968 and 960 cm^{-1}. However, because of the lower yields, the shifted modes of the parent species were not observed in these experiments.

$(C_2H_5)_2O$ + SiF_4. Diethyl ether was codeposited with SiF_4 in argon in two experiments at total dilutions of 1/1/2000 and 1/1/1000. The overall yield of product was decidedly less than in corresponding dimethyl ether experiments at the same concentrations, possibly owing to steric effects with the larger ethyl group. Nonetheless, one product band was observed throughout, in the Si–F stretching region at 965 cm^{-1}, but with a total optical density of less than 0.10. Consequently, additional vibration modes of the trapped species were not detectable.

Discussion

The codeposition of samples of SiF_4 diluted in either argon or nitrogen with any of several oxygen-containing bases gave rise to a number of new infrared absorptions which could not be ascribed to the isolated parent species. For each of the bases H_2O, CH_3OH, $(CH_3)_2O$, and $(C_2H_5)_2O$, the most intense absorption was in the region 960–990 cm^{-1}, with weaker bands occasionally appearing in other spectral regions at higher concentrations. A number of different chemical species might be formed during the deposition process, including the formation of a 1:1 adduct, a 1:2 adduct, or various rearrangement or HF elimination products. Indeed, while more than one product might be formed, examination of band intensities as a function of concentration demonstrates that, in each case, only a *single* product was formed. This is in agreement with early studies involving SiF_4 and NH_3, where only the 1:1 adduct was observed until the matrix material was completely removed and the pure reactants were deposited.

The species formed during deposition could be either the 1:1 adduct or the 1:2 adduct, but it is difficult to envision how a 1:2 adduct might be formed *without* a intermediate 1:1 adduct, particularly at the high dilutions employed. Since only a single species was formed, the 1:1 form is the far more likely choice.

In addition, the spectral features observed lie in a region that has been associated with five-coordinate silicon complexes; six-coordinate (or 1:2) complexes have their most intense absorptions below 800 cm^{-1}, in contrast to the results obtained here. These observations all point to the 1:1 complex, rather than a larger aggregate.

Processes involving HF elimination can also be ruled out on three different grounds. First, HF should be observable in the final spectrum, based upon product yields observed in other spectral regions, yet no HF was detected. Secondly, no known product of HF elimination was detected. For example, Margrave and co-workers[12] have shown that hydrolysis of SiF_4 involves the formation of $(SiF_3)_2O$ and 2HF. The infrared spectrum of $(SiF_3)_2O$ is well known and should be quite intense, yet no evidence of this species was detected. In addition, for several of the bases employed, H_2O and $(CH_3)_2O$ in particular, vibrations of the base subunit in the complex was observed, slightly shifted from the parent. These results suggest that the base is only slightly perturbed in the product species and has maintained its structural integrity, rather than undergoing an elimination or rearrangement reaction. Consequently, HF elimination apparently does not occur under these conditions, and the product formed during the deposition process is most likely the 1:1 adduct between SiF_4 and the oxygen-containing base.

These results indicate the formation of the adducts $SiF_4{\cdot}OH_2$, $SiF_4{\cdot}O(H)CH_3$, $SiF_4{\cdot}O(CH_3)_2$, and $SiF_4{\cdot}O(C_2H_5)_2$, and this represents the first evidence for the existence of these species. For dimethyl ether, a 1:2 adduct had been reported previously, but no spectra had been attained.[10] One sketchy report[13] had also been made of the 1:2 adduct of SiF_4 with H_2O, but little beyond that. A hydrogen-bonded 1:4 complex of SiF_4 with CH_3OH had been suggested in the literature,[14] but no evidence of hydrogen bonding was observed here. The most significant spectral feature of a hydrogen-bonded complex is a dramatic shift to lower energy of the hydrogen stretching frequency, and no such shift was observed.[26] Moreover, the deposition conditions and dilution make formation of a complex as large as a 1:4 adduct very unlikely. In addition, the spectral pattern in the Si-F stretching region was consistent through the entire set of bases, as is discussed below. This strongly suggests the same mechanism of coordination for all of the bases employed, and it would be very difficult to envision a hydrogen-bonding interaction for the hydrogens on dimethyl or diethyl ether. The interaction leading to the stabilization of these 1:1 adducts, rather, must be the donation of electron density from the oxygen to the silicon center on SiF_4, as is well known for nitrogen-containing bases. The structure and bonding in the complexes will be discussed in more detail below. Finally, since this work suggests that a 1:1 complex $SiF_4{\cdot}H_2O$ is stable, one might envision this species as the first intermediate in the hydrolysis of SiF_4, rather than the direct formation of $(SiF_3)_2O$.

It is interesting to compare the codeposition experiments involving SiF_4 and $(CH_3)_2O$ employing a single vs. twin jet arrangement. The yield was found to be comparable with the two different modes of deposition, suggesting that the gas-phase complex is not present in equilibrium to any measurable degree at room temperature. Instead, complex formation occurs on the surface of the matrix, where sufficient thermal energy has been removed from the reactants to stabilize the product complex. Consequently, the lack of observation of these species at room temperature is not surprising.

Band Assignments

Fewer product bands were observed in these experiments with oxygen-containing bases than for the corresponding nitrogen-containing bases. This is presumably due to the lower yield of 1:1 complex, as a consequence of the lesser strength of interaction. Nonetheless, in every system involving an oxygen-containing base and SiF_4, the most intense product band was observed between 984 cm^{-1} (for $H_2O{\cdot}SiF_4$) and 965 cm^{-1} (for $(C_2H_5)_2O{\cdot}SiF_4$). This band often appeared slightly split, or with a weaker satellite within a few cm^{-1} to either higher or lower energy. In addition, when concentrations of reactants were increased to relatively high levels so that product yield was substantial, silicon isotopic bands were observed on this major feature (see, for example, trace d of Figure 1). This indicates that in each case this major product absorption involves a vibration of the silicon atom, and since this region is just below the parent Si–F triply degenerate stretching vibration at 1023 cm^{-1}, this mode is readily assigned to the most intense of the Si–F stretches in the product complex. Moreover, a similar band was observed between 955 and 935 cm^{-1} for all of the methyl-substituted amines and was likewise assigned to the most intense Si–F stretch.

In the amine complexes, this vibration was assigned as the antisymmetric equatorial Si–F stretching mode of a trigonal-bipyramidal complex with the amine in an axial position. For the unsymmetrical (non-C_{3v}) amine bases, this mode was split into a doublet, as a consequence of removal of degeneracy of the equatorial fluorines. The oxygen bases employed here are likewise unsymmetrical (in this sense), and this mode should be a doublet as well, whether the structure is truly trigonal bipyramidal or not (to be discussed below). In each case, a satellite band was observed nearby, usually with considerably lower intensity. This might be assigned either to some site splitting of the primary Si–F stretching band or to the splitting of this mode due to the lack of C_3 symmetry of the base in the complex. Whie this is not readily distinguished, the latter assignment is preferred.

In the amine complexes, a second Si–F stretching mode was observed near 840 cm^{-1}, and in a few of the cases here (notably with CH_3OH) a comparable, relatively weak band was observed in this same region. This analogy suggests assignment to the next most intense of the Si–F stretching vibrations. When concentrations were increased to sufficiently high levels, weak product bands were observed in the region between 400 and 500 cm^{-1}, slightly above the triply degenerate deformation mode of the parent SiF_4 species at 385 cm^{-1}. Medium intensity bands were observed in this region for the $SiF_4{\cdot}$amine 1:1 complexes, and assigned to deformation modes of the SiF_4 subunit within the 1:1 adduct, and a similar assignment for the weak bands in this region in the present experiments is indicated.

In the more concentrated experiments involving SiF_4 and H_2O in either argon or nitrogen matrices, product bands were observed in the O–H stretching and bending regions. In argon, an enhancement of the "rotationless" H_2O bands at 1591 and 3730 cm^{-1} were noted, along with bands which can be assigned to the H_2O subunit in the $H_2O{\cdot}SiF_4$ 1:1 complex. The tightly spaced doublet at 1598 and 1600 cm^{-1} is assigned to the bending mode of H_2O in the complex, while the band at 3722 cm^{-1} is assigned to the antisymmetric stretching mode. Low intensities prevent observation of the symmetric stretching mode of the H_2O unit. Similar results were observed in nirogen matrices, where H_2O rotation does not occur (and hence simpler spectra) but the overall yields were generally lower.

When $(CH_3)_2O$ was complexed with SiF_4 in argon matrices, bands were observed near many of the parent vibrations of $(CH_3)_2O$, as is typified by the bands of 917 and 3006 cm^{-1}, shown in Figure 4. These are assigned to the vibrations of the dimethyl ether subunit in the 1:1 complex with SiF_4, and the relatively small shift away from the positions of the free parent molecule is suggestive of a quite weak interaction, as is anticipated for these complexes. It is interesting to note that no such perturbed modes of CH_3OH in the $CH_3OH{\cdot}SiF_4$ adduct were observed, despite careful comparison to the blank spectrum of CH_3OH in argon. This may be due to the fact that CH_3OH dimerizes quite readily (compared, for example, to $(CH_3)_2O$), and consequently the parent spectrum is substantially more complex. Moreover, the strength of interaction between CH_3OH and SiF_4 is likely to be similar to the strength of interaction between CH_3OH units in the dimer, and hence shifts of the vibrational frequencies of the CH_3OH units in the dimer and in the 1:1 SiF_4 adduct will be similar (except for the hydrogen stretching vibration, which is hydrogen-bonded in the CH_3OH dimer and should show a large shift). Consequently, perturbed parent vibrations of the CH_3OH subunit in

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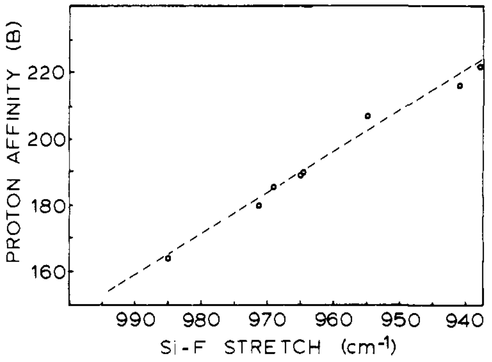

Figure 5. Plot of the position of the most intense Si–F stretching vibration of SiF_4 in SiF_4·B complexes, vs. the proton affinity of the base B.

Table I. Correlation of Si-F Stretching Frequencies in 1:1 SiF_4·B Complexes with Proton Affinities of the Base B

PA,[a] kcal/mol	Si-F, cm^{-1}	base	ref
222	936	$(CH_3)_2NH$	8
216	941	$(CH_3)NH_2$	8
207	955	NH_3	7
190	964	$(CH_2)_3O$	17
189	965	$(C_2H_5)_2O$	*b*
186	969	$(CH_3)_2O$	*b*
180	973	CH_3OH	*b*
166	984	H_2O	*b*

[a] Reference 27. [b] This work.

the CH_3OH·SiF_4 complex may be hidden by the bands due to the CH_3OH dimer. Finally, with $(C_2H_5)_2O$, the yield of product was sufficiently low that no perturbed base vibrational modes were detected.

Structure and Bonding

The 3*N* - 6 vibrations of a Lewis acid–base complex can be divided into three categories: (1) the vibrations of the acid subunit, (2) the vibrations of the base subunit, and (3) the vibrations (stretching and deformation) of the acid subunit against the base, which arise from loss of rotational and translational degrees of freedom during complex formation. The former two types of vibrations were observed for the complexes studied here, while the last category was probably too low in frequency to be observed. Of the vibrational modes observed, it is apparent that the modes of the Lewis acid, SiF_4, are more strongly shifted than those of the various bases. Consequently, any attempt to correlate the spectroscopic results here might well be based on the SiF_4 vibrations in the complex and, in particular, the most intense Si–F stretching vibration. This mode, occurring in the 970-cm^{-1} region, did shift as the base was altered, and in a systematic fashion. Using gas-phase proton affinities of the bases[27] as a measure of inherent basicity, a monotonic, nearly linear correlation was observed. The band position of the Si–F stretch for various base complexes is plotted in Figure 5 against proton affinity of the base, and it is clear that increasing base strength decreases the frequency of the most intense Si–F stretch (see also Table I). These data suggest that SiF_4 is a π^* acceptor,[28] and that dπ–pπ interaction between the empty silicon d orbitals and the filled p orbitals on the fluorine is disrupted as the complex forms and the geometry of the SiF_4 subunit is altered. This is similar to the result observed for complexes of BF_3, where the pπ–pπ bonding between the boron and the fluorines is disrupted by complex formation. The B–F stretching frequency decreases from around 1450 cm^{-1} for free BF_3 to 1200 cm^{-1} for the BF_3·$O(CH_3)_2$ adduct, and to 1150 cm^{-1} for the BF_3·NH_3 adduct.[29–31] In these complexes, it has also been noted that as the B–N distance shortens, the B–F distances increase and the F–B–F angles decrease.[32] Interestingly, a stronger interaction[33] is noted for oxygen complexes of GeF_4, where the dπ–pπ is not expected to be as strong owing to the larger more diffuse orbitals on germanium as opposed to silicon.

Symmetry arguments were put forward to support a C_{3v} structure for the SiF_4·NH_3 complex, and a reduction in symmetry was observed for the unsymmetrical bases CH_3NH_2 and $(CH_3)_2NH$. Less can be concluded concerning the structure of the weakly bound complexes reported here. The bases employed are themselves relatively unsymmetrical, so a strictly trigonal-bipyramidal structure is not possible. Even then, an insufficient number of vibrational modes were detected to draw firm conclusions about the structure of the complex. It is likely, in view of the similarity of spectra for all of the adducts, including the amines, that the perturbation of the SiF_4 unit is in the direction of a trigonal bipyramid, but that this limit is reached only for the amine complexes. Nonetheless, the sharpness of the product bands is suggestive of a distinct specific interaction with the formation of a weak coordinate bond between the SiF_4 unit and the oxygen atom of the base, rather than simply a perturbation caused by trapping in adjacent matrix sites.

Conclusions

The work presented in this manuscript demonstrates that 1:1 complexes between SiF_4 and oxygen-containing bases can be formed and characterized under the appropriate experimental conditions. These complexes are spectroscopically similar to analogous complexes with nitrogen-containing bases, but the overall yield was lower. The band position of the most intense Si–F stretching mode of the SiF_4 subunit in the complex was noted to vary linearly with the basicity of proton affinity of the Lewis base donor, suggesting that SiF_4 is a π^* acceptor. Perhaps these results will generate further interest in the study, both experimental and theoretical, of relatively weakly bound molecular complexes.

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Registry No. SiF_4·OH_2, 86542-57-6; SiF_4·$O(H)(CH_3)$, 86542-58-7; SiF_4·$O(CH_3)_2$, 86542-59-8; SiF_4·$O(C_2H_5)_2$, 86542-60-1.

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