Matrix Isolation Spectroscopic Study of the 1:1 Complexes of TiF_4 with NH_3 and $(CH_3)_3N$

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The matrix isolation technique with twin-jet deposition has been coupled with infrared spectroscopy for the isolation, identification, and characterization of the 1:1 complexes of TiF_4 with NH_3 and $(CH_3)_3N$. For each of these complexes, two perturbed Ti−F stretching modes were observed to be red-shifted 40−90 cm^{-1} from the triply degenerate parent TiF_4 mode at 792 cm^{-1}, indicating a reduction of symmetry in the complex to at least C_{3v}. In addition, the symmetric deformation mode of the NH_3 subunit shifted 228 cm^{-1} to higher energy, indicating that TiF_4 is a moderate strength Lewis acid. Merged jet deposition of these reagents led to no observed product in the matrix and no parent TiF_4, suggesting that a reaction to form a nonvolatile product in the merged or reaction region had occurred, probably forming the very stable 1:2 complex.

Introduction

Titanium tetrafluoride is well-known as a moderate strength Lewis acid, one that forms relatively stable 1:2 complexes with a variety of electron donors. Many of these were characterized spectroscopically in the late 1950s and early 1960s.[1−6] TiF_4 is also known to be a rapid scavenger of NH_3, although no complexes of TiF_4 and NH_3 have been identified. By analogy to these early studies, a 1:2 complex in a cis octahedral arrangement would be expected. TiF_4 complexes of the 1:1 type are much rarer, forming only with tertiary amine donors with large steric requirements. Even then, these complexes are believed to be polymeric in the solid state.[1] At the same time, one must anticipate the formation of a 1:1 complex as a short-lived intermediate in the formation of the stable 1:2 complex (i.e., that the ligands add sequentially). For TiF_4, such transient intermediates have not been observed.

The matrix isolation technique[7−9] was developed in the mid-1950s as a mean for the isolation, stabilization, and characterization of reactive intermediates, including radicals, ions, and molecular complexes. This technique has been employed over the years to study a wide range of molecular species. Of particular relevance here is the analogous SiF_4/NH_3 system where the 1:2 complex with NH_3 was very well-known, and the 1:1 complex was observed in this laboratory[10] after isolation in argon and nitrogen matrixes. This complex was found to be trigonal bipyramidal with the NH_3 ligand in an axial position, in contrast to expectations. Since then, several theoretical calculations have confirmed this geometry.[11,12] Matrix isolation provides a method by which intermediate complexes of TiF_4 may be formed, isolated, and characterized. Consequently, a study was undertaken to examine the species formed in the reactions of TiF_4 with NH_3 and $(CH_3)_3N$.

Experimental Section

All of the experiments in this study were carried out on conventional matrix isolation equipment that has been described previously.[13,14] NH_3 (Matheson), $^{15}NH_3$ (Cambridge Isotope Laboratory, 99% ^{15}N), and $(CH_3)_3N$ (Aldrich) were introduced into the vacuum systems from lecture bottles and purified by freeze−pump−thaw cycles at 77 K. TiF_4 is a solid at room temperature and was placed in a small glass sidearm connected to the deposition line by an Ultratorr tee. Once under vacuum, the solid material (Aldrich) was heated to approximately 100 °C. At this temperature, TiF_4 has a small vapor pressure that was swept by flowing argon and carried to the cold cell. The length of deposition line from the tee to the cold cell was wrapped with heating tape and was held at a temperature somewhat higher than 100 °C to prevent deposition of the TiF_4 vapor on the walls of the deposition line.

Matrix samples were deposited in both the twin jet and merged jet modes. In the former, the amine was diluted in argon in one manifold and the argon was introduced into a separate manifold. These two samples were sprayed simultaneously on the cryogenic surface from separate nozzles after the pure argon stream passed over the heated TiF_4. This allows for only a very brief mixing and reaction time before matrix deposition. In the merged jet experiments,[14] the Ar and Ar/amine gas samples were again prepared in separate manifolds. The two deposition lines were then joined with an Ultratorr tee at some distance from the cryogenic surface and *downstream* from the sidearm containing the TiF_4(s). The Ar/TiF_4 and Ar/amine samples flowed together through the joined or “merged” length, allowing for increased reaction time compared to twin-jet deposition, but without the static equilibration that occurs with single jet deposition. The length of the merged region or reaction zone could be adjusted from as short as 10 cm to as long as 250 cm. Samples were deposited at a flow rate of approximately 2 mmol/h from each manifold for a period of 20−24 h. Infrared spectra were recorded at intervals during deposition as well as at the end of the deposition period. Spectra were recorded on a Mattson Cygnus FTIR at a resolution of 1 cm^{-1} over the range 400−4000 cm^{-1}.

Results

Prior to any co-deposition experiments, blank experiments were run on each of the reagents alone in argon at several different concentrations. The blank spectra of NH_3, $^{15}NH_3$, and $(CH_3)_3N$ were all in good agreement with literature spectra[15,16] and spectra recorded previously in this laboratory. A spectrum of TiF_4 has been reported[17] in a neon matrix at 799 cm^{-1}, but no previous reports in solid argon were found. The blank

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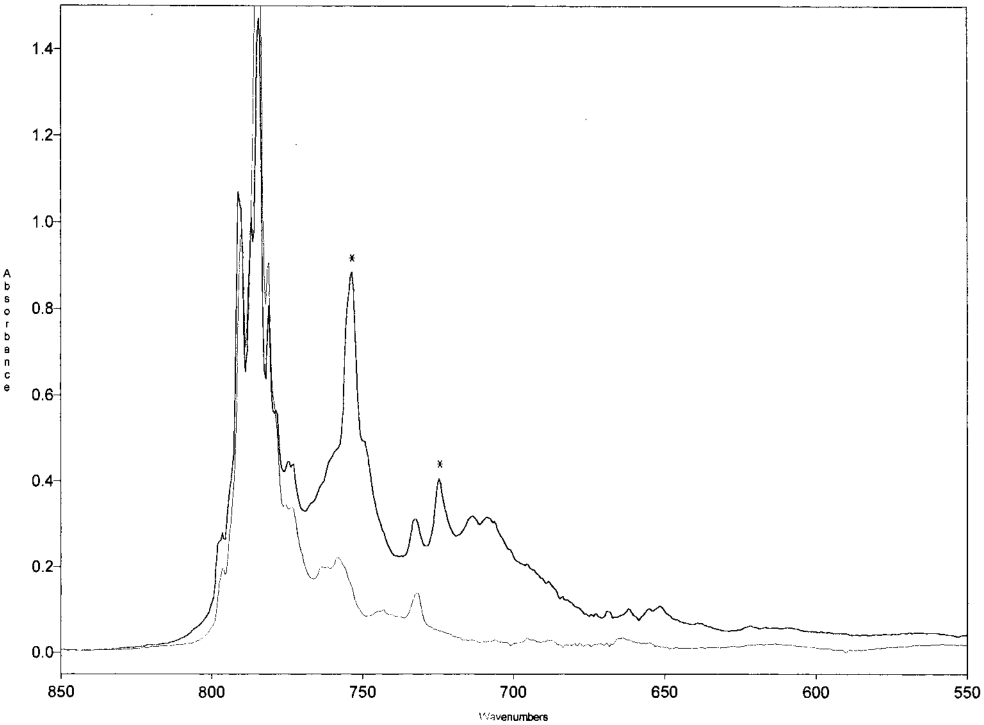

Figure 1. Infrared spectrum between 550 and 850 cm^{-1} of a matrix prepared by twin jet co-deposition of a sample of Ar/TiF_4 with a sample of Ar/NH_3 = 250 (upper trace) compared to a blank spectrum of Ar/TiF_4 (lower trace). Bands denoted with an * are assigned to the 1:1 complex TiF_4·NH_3.

experiments showed a very intense absorption at 792 cm^{-1} with some splitting due to titanium isotopes in natural abundance. A shift of 7 cm^{-1} to lower energy from neon to argon (and 8 cm^{-1} from the gas phase[18,19] to argon) is very reasonable for a nonpolar molecule such as TiF_4 and is assigned to ν_3, the triply degenerate stretching mode of the tetrahedral molecule. Additional weak features were observed in some blank experiments to the red side of the intense parent band. These were variable in intensity and may be due either to a small amount of aggregation or to interaction with impurity H_2O. Weak bands were also noted above 3900 cm^{-1} and are due to HF, the hydrolysis product of TiF_4.

TiF_4 + NH_3. These two reagents were co-deposited in the twin jet mode into argon matrixes in a large number of experiments over a wide range of concentrations. While preparation of Ar/NH_3 samples of known concentration was straightforward, control of the rate of sublimation of TiF_4 was more difficult to attain and impossible to quantify. Thus, experiments were run such that the 790 cm^{-1} band of parent TiF_4 was as strong as 2.5 OD after 20 h of deposition in the most concentrated samples and as weak as 0.2 OD in the least concentrated samples. The Ar/NH_3 ratios varied from 1000/1 to 250/1. In all of the twin jet co-deposition experiments, several new infrared absorptions were noted, at 725, 755, 917, 1094, 1679, and 3041 cm^{-1}, in addition to a weak multiplet centered at 1202 cm^{-1}, as shown in Figures 1 and 2. A weak, broad feature was also seen around 710 cm^{-1} in some experiments, particularly those with relatively high NH_3/TiF_4 ratios. The intensities of all of these bands increased as the NH_3 concentration was increased. On the other hand, the bands at 725, 755, and 1202 cm^{-1} (hereafter referred to as set A) increased monotonically with increasing levels of TiF_4, while the bands at 917, 1094, 1679, and 3041 cm^{-1} (hereafter referred to as set B) did not show a clear dependence on the level of TiF_4. Over this extensive set of experiments, the bands in set A appeared to maintain a constant intensity ratio to one another, but not to the bands in set B. However, the set B bands did maintain a constant intensity ratio with respect to one another.

Additional twin jet experiments were conducted with TiF_4 and samples of Ar/$^{15}NH_3$, over the concentration range 250/1 to 500/1. Again, a range of TiF_4 levels were employed by varying the sublimation temperature slightly. Product bands were noted at 725, 755, 917, 1090, and 3041 cm^{-1} along with a weak multiplet centered at 1197 cm^{-1}. These absorptions were reproducible in all of the experiments; the set at 725, 755, and 1197 cm^{-1} (the ^{15}N counterparts of set A) maintained a constant intensity ratio with respect to one another, but not to the bands at 917, 1090, and 3041 cm^{-1} (counterparts to the set B bands). As noted above, these latter bands did maintain a constant intensity ratio with respect to one another.

Merged jet experiments were also conducted with samples of Ar/NH_3 = 250 and Ar/TiF_4, over a range of sublimation temperatures. In several such experiments, the 792 cm^{-1} band due to parent TiF_4 was not observed and the set A bands were not present in the spectrum. The bands of parent NH_3 were somewhat reduced, and the bands of set B were still present, but weak. In two of these experiments, a spectrum was recorded after 10 h of deposition. When this spectrum showed no set A bands and no bands due to parent TiF_4, the Ar/NH_3 stream was shut off for the next 10 h period. The 792 cm^{-1} band of to parent TiF_4 then grew in very strongly after the Ar/NH_3 gas flow was stopped, indicating that sublimation was taking place.

TiF_4 + $(CH_3)_3N$. TiF_4 was sublimed and co-deposited in the twin jet mode with samples of Ar/$(CH_3)_3N$ = 250 in several experiments. Distinct new product features were noted at 701, 741, 817, 1006, 1115, 1215, 1870, 1898, 2548, and 2589 cm^{-1}. Figure 3 shows the spectrum in the low-energy region of a typical matrix containing these reagents. The intensities of these bands were studied as a function of $(CH_3)_3N$ concentration and TiF_4 level. The bands at 701, 741, 817, and 1006 cm^{-1} (hereafter set C) maintained a constant intensity ratio with respect to one another, but not with respect to the remaining

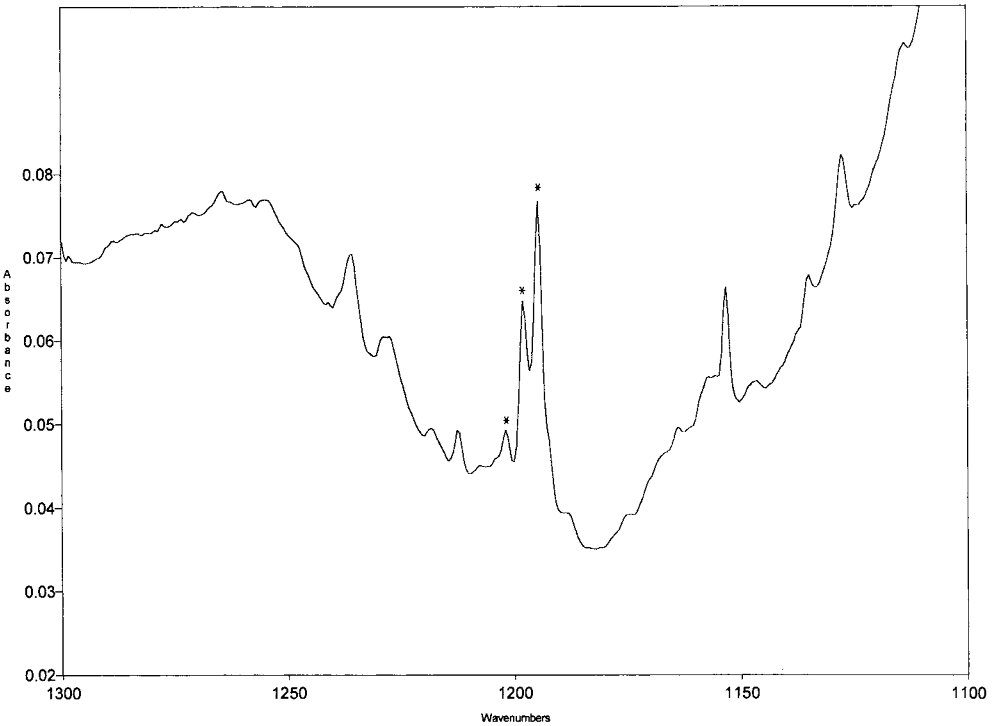

Figure 2. Infrared spectrum, from 1100 to 1300 cm^{-1}, of a matrix prepared by the twin jet co-deposition of a sample of Ar/TiF_4 with a sample of $Ar/NH_3 = 250$. Bands denoted with an * are assigned to the 1:1 complex $TiF_4 \cdot NH_3$.

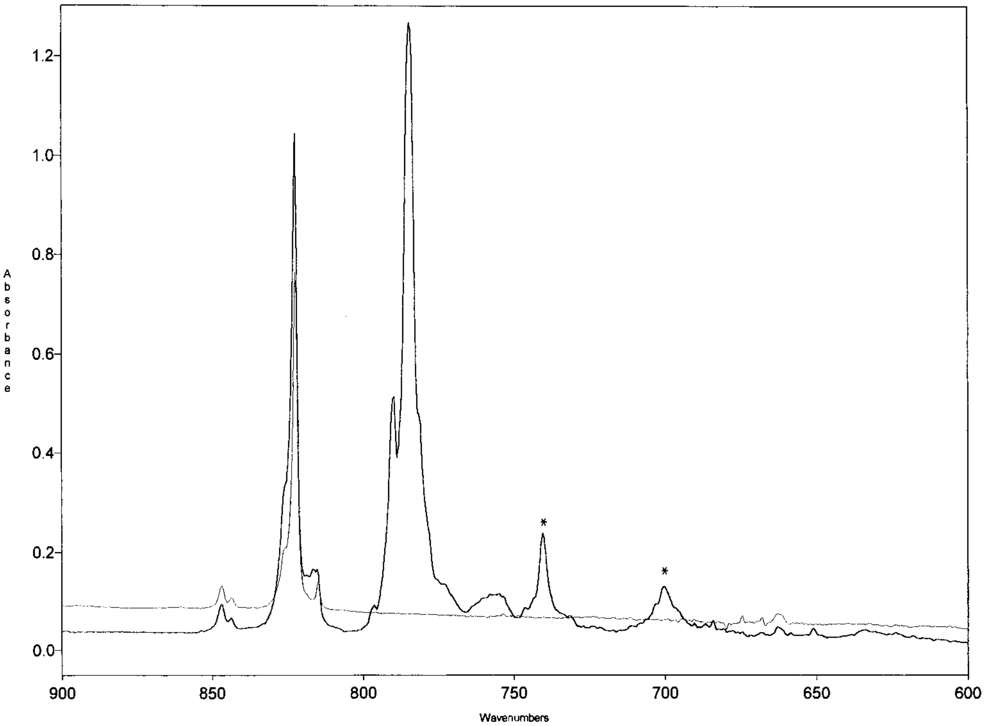

Figure 3. Infrared spectrum between 600 and 900 cm^{-1} of a matrix prepared by twin jet co-deposition of a sample of Ar/TiF_4 with a sample of $Ar/(CH_3)_3N = 250$ (upper trace) compared to a blank spectrum of $Ar/(CH_3)_3N = 500$ (lower trace). Bands denoted with an * are assigned to the 1:1 complex $TiF_4 \cdot (CH_3)_3N$.

bands. The intensity of the remaining bands depended directly on the $(CH_3)_3N$ concentration, but not directly on the TiF_4 level. Additionally, two merged jet experiments were conducted with this pair of reagents. In the first, no product bands in set C were observed, while the remaining bands were weakly present. The 792 cm^{-1} band of parent TiF_4 was also absent. In the second experiment, a spectrum was taken after 10 h of deposition. This spectrum did not contain the bands of set C, and it did not contain the intense 792 cm^{-1} band of parent TiF_4. At this point, the $Ar/(CH_3)_3N$ gas flow was stopped and the Ar/TiF_4 flow continued. The 792 cm^{-1} band of parent TiF_4 then grew rapidly in intensity over the remaining 10 h of deposition.

Discussion

As noted above, a number of new infrared absorptions were noted in the twin-jet deposition of TiF_4 with NH_3 into argon matrixes. These could be divided into two groups, A and B, as a result of intensity variation over a number of experiments at different reagent concentrations. Set B is readily identified by comparison to the literature[20a] as the 1:1 complex of HF with NH_3. HF is a low level impurity in all experiments involving TiF_4 and since this complex forms readily, its presence is anticipated. Further, the set B bands did not show a clear dependence on the level of TiF_4 in the matrix, indicating that the species responsible for the bands of set B does not require TiF_4 for formation (other than the fact that the low HF levels in these experiments comes from slight hydrolysis of the TiF_4 solid in the sidearm).

The set A bands, at 725, 755, and 1202 cm^{-1}, showed a monotonic dependence on the concentration of both NH_3 and TiF_4, indicating that both are required for the formation of this species. The 1202 cm^{-1} band showed a 5 cm^{-1} shift with ^{15}N substitution, while the lower two bands did not shift with ^{15}N substitution. The 5 cm^{-1} shift of the 1202 cm^{-1} band is very similar to the ^{15}N shift of the symmetric and antisymmetric deformation modes of parent NH_3 (4 and 5 cm^{-1} shifts, respectively) and thus is consistent with substantial nitrogen atom participation in the vibration. The lack of ^{15}N shift for the two lower product bands demonstrates that the nitrogen atom does not participate in those vibrational modes, strongly suggesting that they are Ti$-$F stretching modes. It should also be noted that the HF levels in these experiments did not increase from the TiF_4 blank to the co-deposition runs, demonstrating that HF is not a product in this reaction.

The observations in the preceding paragraph are consistent with and lend strong support to the formation of a molecular complex. First, essentially any further reaction between these reagents would produce HF. Second, in a molecular complex, the two subunits (NH_3 and TiF_4 in this case) are perturbed and key vibrational modes shifted. Complexes of NH_3 are predominantly characterized by a blue-shift of the ν_2 symmetric deformation or umbrella mode, up to as high as 1300 cm^{-1} for strong complexes.[21] The 1202 cm^{-1} product band, with its 5 cm^{-1} ^{15}N shift, is readily assigned as the symmetric deformation mode of NH_3 in a molecular complex with TiF_4. On the other hand, the stretching modes of the Lewis acid in the complex are shifted to lower energy as a consequence of electron donation to the Lewis acid. The bands at 725 and 755 cm^{-1} are clear candidates for shifted TiF_4 stretching modes, to the red of the 792 cm^{-1} parent band. This parent mode is triply degenerate as a consequence of the tetrahedral symmetry. In the complex, the symmetry is reduced and a splitting of this mode into at least two components is anticipated. If the symmetry is reduced to C_{3v}, then the F_2 mode of the parent must split into two modes, of E and A_1 symmetries. Also, the forbidden A_1 symmetric stretching mode of the parent, known to lie at 712 cm^{-1} from Raman studies,[22] should be activated. However, in a weakly bound complex, the perturbation is weak and this mode may not be detectably activated. If the symmetry of the complex were less than C_{3v}, then four distinct Ti$-$F stretching modes are allowed. However, the relative intensities of these modes are not readily determined. The bands at 725 and 755 cm^{-1} are appropriate for two Ti$-$F stretching modes. These facts, combined with the known propensity of TiF_4 to form molecular complexes with Lewis bases, support the conclusion that a molecular complex is formed between TiF_4 and NH_3 in these experiments and that this complex is responsible for the 725, 755, and 1202 cm^{-1} absorptions.

The stoichiometry of the complex is less readily determined, since an intermediate 1:1 complex is anticipated and the stable product in this system is likely the 1:2 complex. However, it should be noted that only a single product was observed over a wide concentration range, including at very low NH_3 concentrations and relatively high TiF_4 concentrations (i.e., a high TiF_4/NH_3 ratio). If a 1:2 complex formed in these experiments, one would expect to see both the 1:1 and 1:2 complex under different conditions, yet only a single product was formed, other than the weak broad feature near 710 cm^{-1} that tended to be more prominent at higher NH_3 concentrations. Also, the complex was formed only in the twin jet mode, where the mixing time is very brief. In the analogous SiF_4/NH_3 system, where the 1:2 complex is very well-known and stable, only the 1:1 complex was isolated under twin jet conditions.[10] All of these points argue that the stoichiometry of the molecular complex observed here between TiF_4 and NH_3 is 1:1, and thus the 725, 755, and 1202 cm^{-1} bands are assigned to the argon matrix-isolated 1:1 complex $TiF_4{\cdot}NH_3$. The band at 710 cm^{-1} observed in some experiments may be due to a small amount of the 1:2 complex, particularly since it was most prominent in experiments with a high NH_3/TiF_4 ratio. However, without the observation of additional bands, this assignment must be regarded as tentative.

Additional vibrational modes for a 1:1 complex are anticipated, in addition to the three bands observed here. As noted above, either three or four Ti$-$F stretching modes are infrared active, depending on the symmetry of the complex, while two were observed. The remaining one or two Ti$-$F stretching modes are very likely too weak to be observed. Of course, the TiF_4 bending modes are also perturbed in the complex. However, for the parent compound these lie near 200 cm^{-1}, well below the 400 cm^{-1} cutoff of the spectrometer used for the present study. Additional perturbed vibrational modes of the NH_3 subunit are anticipated as well. However, many previous studies of NH_3 complexes in matrixes and in the solid state have shown that the ν_2 symmetric deformation mode is much more sensitive to complexation than the stretching or antisymmetric bending modes are. Thus, the other modes probably did not shift measurably out from under the intense parent modes observed in these experiments. Finally, formation of a complex from two species leads to a loss of three rotational and three translational degrees of freedom. These become vibrational modes in the complex, all involving the motions of one subunit relative to the other. However, in a weakly bound complex, these will all lie at very low energies, below the lower spectral limit in this study.

It is noteworthy that in the merged jet experiments, no products were observed at all, despite the presence of TiF_4 and NH_3 in the reaction zone. This demonstrates that the reaction between these two species is very rapid and a nonvolatile product is formed in the reaction zone and is deposited on the walls of the reaction zone prior reaching the matrix. The identity of this nonvolatile product cannot be determined, but given the strong affinity of TiF_4 for NH_3, the fact that additional HF product was not observed and the known propensity of TiF_4 to form 1:2 complexes with strong electron donors it is likely that the product formed and deposited on the wall of the reaction zone is the 1:2 complex $TiF_4{\cdot}2NH_3$.

Similar experiments with TiF_4 and $(CH_3)_3N$ led to comparable results, with two sets of product bands. One set can be readily identified as the 1:1 complex of $(CH_3)_3N$ with HF by comparison to literature spectra.[20b] The second set, set C, contained two product bands in the Ti$-$F stretching region, at 701 and 741 cm^{-1}, and two bands near modes of parent $(CH_3)_3N$, at 817 and 1006 cm^{-1}. By use of the arguments presented above for

TABLE 1: Comparison of the Band Position of the Symmetric Deformation Mode of NH_3 in Matrix Isolation Complexes

complex	band position (cm^{-1})	reference
	974	a
SO_2	1038	24
$(CH_3)_2Cd$	1044	25
ClF	1050	26
$(CH_3)_2Zn$	1087	27
$(CH_3)_3In$	1119	28
TiF_4	1202	a
$(CH_3)_3Ga$	1203	29
SiF_4	1253	10
SO_3	1317	30

[a] This work.

NH_3, these bands are assigned to the isolated 1:1 complex $TiF_4 \cdot N(CH_3)_3$. Trimethylamine is known to be a stronger base than ammonia, based on gas-phase proton affinities,[23] thus more electron density should be transferred to the TiF_4 subunit in the complex and a greater red-shift would be anticipated for the two Ti−F stretching modes, as observed. The two $(CH_3)_3N$ modes that were perturbed in the complex were also perturbed in the $(CH_3)_3N \cdot HF$ complex (although to a different degree), lending further support to the conclusion that complex formation had occurred.

Merged jet experiments on the $TiF_4/(CH_3)_3N$ system led to very similar results as those observed for the TiF_4/NH_3 system, namely complete absence of TiF_4 and any product in the resulting matrix. Again, it appears that formation of a nonvolatile product is occurring in the reaction zone, a product that may well be the 1:2 complex. However, insufficient data is available to permit a definite conclusion on this point.

Comparison to similar complexes, particularly of NH_3 with Lewis acids, is of interest as well. As noted above, the symmetric deformation mode ν_2 of NH_3 is very sensitive to complexation, and the magnitude of the shift to higher energy has often been correlated with the strength of this interaction. Table 1 compares the position of ν_2 for a number of 1:1 complexes of NH_3 that have been studied in argon matrixes. Clearly, the shift in the present TiF_4 complex is larger than many, although not as large as the shifts caused by the very strongly Lewis acidity of SO_3 and SiF_4. Thus, on a scale of Lewis acidities, using the shift of ν_2 as a criterion, TiF_4 is a moderately strong Lewis acid, in keeping with the known solution chemistry of TiF_4. At the same time, it is surprising that the overall yield of the molecular complex was relatively low, when no distinct barrier to complex formation is anticipated. For example, the overall intensities of the 1:1 complex, including the symmetric deformation mode of NH_3, were quite a bit less than those for the $SiF_4 \cdot NH_3$ complex. This result may be due to differences in deposition geometry that affect the already very brief mixing time during twin-jet deposition.

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