

# Rotational spectra, dipole moment, and structure of the SiF<sub>4</sub>-NH<sub>3</sub> dimer

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Rotational spectra of several isotopic species of the SiF<sub>4</sub>-NH<sub>3</sub> dimer were obtained with the Mark II Flygare-Balle FT-MW spectrometer. This is the first determination of the gas phase structure of a penta-coordinated silicon. The spectra indicate a symmetric top, trigonal bipyramid SiF<sub>3</sub>N structure with the lone electron pair of the NH<sub>3</sub> pointed at one face of the SiF<sub>4</sub> and the three equatorial F's splayed significantly away from the N. The  $\angle F_{ax}-Si-F_{eq}$  is about 12° less than tetrahedral. The Si-N distance is determined to be 2.090 Å. The experimental results are in excellent agreement with the SiF<sub>4</sub> deformation predicted by the *ab initio* calculations of Rossi and Jasinski [Chem. Phys. Lett. **169**, 399 (1990)]. The measured dipole moment is 5.61 D, an enormous enhancement compared to the sum of the monomer moments, 1.47 D. The increase of 4.14 D is due largely to the geometric distortion of the tetrahedral SiF<sub>4</sub> molecule upon dimer formation, demonstrating that the Si-F bond is much more ionic than covalent. If the charge is simply partitioned between Si and F so as to obtain a moment of 4.14 D, the Si has a charge of +3.52 and each F, -0.88. This conclusion is consistent with recent applications of the atoms-in-molecules charge partition methodology developed by Bader and co-workers.

## INTRODUCTION

The first gas phase structure of a penta-coordinated Si is reported herein, with results indicating highly polar Si-F bonds. A large number of structural determinations of penta-coordinated Si in crystal silatranes have been made by Voronkov and co-workers and the properties of the compounds reviewed.<sup>1</sup> The silatranes (cyclic organosilicon ethers of tris amines) have a relatively strong intramolecular bond between Si and N, with an enthalpy on the order of 5 to 15 kcal. Similarities in structure, dipole moment, and Si-N bond enthalpy between silatranes and SiF<sub>4</sub>-NH<sub>3</sub> suggest a possible reinterpretation of the nature of chemical bonding in silatranes, based on the results obtained for SiF<sub>4</sub>-NH<sub>3</sub>. Various concepts have been used to explain bonding at the pentacoordinated Si in silatranes, among them hybridization and hypervalency arguments. A simpler picture based on highly ionic bonds is feasible.<sup>2</sup>

Recent *ab initio* calculations<sup>3-5</sup> suggested that the SiF<sub>4</sub>-NH<sub>3</sub> dimer could be observed with the FT-MW, free jet spectroscopy technique. Several factors motivated us to determine its structure. One might expect that the interplay between *ab initio* theory and experiment would reveal limitations of either or both approaches, as well as enhance understanding of the nature of bonding in the dimer. For example, it has recently been suggested that the Si-F and Si-H bonds in SiF<sub>4</sub> and SiH<sub>4</sub> are better described as mostly ionic rather than covalent.<sup>6</sup> *Ab initio* calculations indicate that the  $F_{eq}-Si-F_{ax}$  angle, equal to the tetrahedral angle 109.47° in

unperturbed SiF<sub>4</sub>, is greatly changed, to about 97°, upon formation of the Si-N bond in the SiF<sub>4</sub>-NH<sub>3</sub> dimer.<sup>3</sup> The effect this geometrical distortion has on the dipole moment of SiF<sub>4</sub>-NH<sub>3</sub> will be much larger if the Si-F bonds are strongly ionic than if they are strongly covalent. If the dipole moment of the dimer is indeed much greater than that of free NH<sub>3</sub>, it would support the recent analysis of Si-F bond type,<sup>6</sup> based on the methodology developed by Bader and co-workers<sup>7-9</sup> for assigning charges to atoms in molecules.

Previous work related to the SiF<sub>4</sub>-NH<sub>3</sub> dimer includes matrix ir spectra, which were interpreted as suggesting, but not proving, C<sub>3v</sub> symmetry.<sup>10</sup> The 1:1 and 1:2 adducts of SiF<sub>4</sub> with N(CH<sub>3</sub>)<sub>3</sub> have been studied in the solid phase and dissolved in benzene, by ir and Raman spectroscopy.<sup>11</sup> The spectra of the adducts were also interpreted as suggesting but not proving C<sub>3v</sub> symmetry. Vapor pressure measurements on the solid SiF<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>, first discovered in 1812,<sup>12</sup> yield a molar dissociation enthalpy of 9.1 kcal per Si-N bond.<sup>13</sup> Similar measurements on solid SiF<sub>4</sub>-NH<sub>3</sub> allow assignment of an upper bound of 13.7 kcal for the dissociation enthalpy of the Si-N bond.<sup>14</sup> The one x-ray diffraction crystal structure determination of an adduct is for SiF<sub>4</sub>(pyridine)<sub>2</sub>.<sup>15</sup> The structure determined has a square planar SiF<sub>4</sub> with a pyridine on either side and a Si-N bond length of 1.93 Å. The x-ray powder diffraction pattern of SiF<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub> has been reported, but not the crystal structure.<sup>13</sup> Si-N bond distances in the various beautiful silatrane molecules, determined by x-ray diffraction, vary between 2.0 and 2.2 Å (Ref. 1).

SiF<sub>4</sub> and NH<sub>3</sub> form a solid at room temperature, SiF<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>, which has a 298 K vapor pressure of about 16 mTorr.<sup>13</sup> This low vapor pressure suggested that premixing the gases SiF<sub>4</sub> and NH<sub>3</sub> in the usual way used for miscible

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gases would likely not work. The technical challenge presented would be a good test for a new coaxial mixing nozzle, recently employed in the determination of the structure of the H-bonded heterotrimer NH<sub>3</sub>-HCN-HF.<sup>16</sup> These and other aspects of the structure of the SiF<sub>4</sub>-NH<sub>3</sub> dimer are discussed below.

Lastly, the SiF<sub>4</sub>-NH<sub>3</sub> dimer was seen as a prototype for observation of the significantly less stable SiH<sub>4</sub>-NH<sub>3</sub>. This dimer has been indirectly observed via mass spectrometric techniques<sup>17</sup> and theoretically predicted to be stable only at the highest level of *ab initio* theory.<sup>3</sup> It is predicted to have the same symmetry as SiF<sub>4</sub>-NH<sub>3</sub>. The rotational spectrum and structure of the SiH<sub>4</sub>-NH<sub>3</sub> dimer will be reported separately.<sup>18</sup>

## EXPERIMENT

The Flygare-Balle Mark II FT-MW spectrometer with pulsed valve and large Fabry-Perot cavity has been previously described.<sup>19</sup> Improvements that aided observation of the SiF<sub>4</sub>-NH<sub>3</sub> rotational spectra include an Autosearch computer program recently added to the system. It enables searches for new transitions to be made over intervals of ~50 MHz in a series of automatic steps (0.4 MHz). The Autosearch program,<sup>20</sup> in fact, found the first SiF<sub>4</sub>-NH<sub>3</sub> transition,  $J=0$  to 1 with several hyperfine components, while Ruoff and Gutowsky were discussing collisional processes in free jets and not watching the spectrometer closely at all. The benefit to the operator is that other experimental parameters such as gas flows, valve performance, etc., can be monitored as the spectrometer searches. Also, the program does not lose patience.

Initially, SiF<sub>4</sub> and NH<sub>3</sub> were premixed in a gas manifold developed by Emilsson.<sup>21</sup> In this manifold the gas concentrations are determined by calibrated flow meters (MKS, Inc.), and it is not necessary to make dilute mixtures in helium prior to mixing because the flow meters can be set for very low flow rates. It became clear that premixing the gases was not working because of buildup of a white powder. To avoid this problem, a coaxial nozzle was employed. The arrangement allows one to control the mixing time of reactive components by injecting one at an adjustable point directly into the free jet expansion region.<sup>16</sup> All of the spectra reported here were obtained with the coaxial nozzle.

SiF<sub>4</sub> (Matheson, 99.9% pure) and NH<sub>3</sub> (Matheson) were used as obtained from the manufacturer. The <sup>15</sup>NH<sub>3</sub> was supplied by Icon Services, Inc. First run neon (Airco) was used as a carrier gas, with a typical backing pressure of 2 atm behind the nominally 0.75 mm orifice. The orifice size is difficult to specify because the thin coaxial injection tube protrudes through it.

## RESULTS AND ANALYSIS

### Spectra

The objectives of this study were to determine the structure and dipole moment of the SiF<sub>4</sub>-NH<sub>3</sub> dimer. In practice two features of the structure caused some problems in its determination. The silicon atom is very close to the center of

mass (c.m.) of the dimer. Therefore, the location of the silicon is harder to find accurately and the transitions for the three silicon isotopes (<sup>28</sup>Si, 92%; <sup>29</sup>Si, 5%; <sup>30</sup>Si, 3%) badly overlap. Moreover, the barrier to internal rotation of the NH<sub>3</sub> molecule is small, producing transitions of excited internal rotation states which further congest the spectra,<sup>22</sup> even at the low temperature of our jet expansion. The hyperfine interactions also caused trouble. The largest is the <sup>14</sup>N quadrupole interaction which produces hyperfine structure (hfs) giving useful information about the torsional mobility of the NH<sub>3</sub>. But no attempt was made to analyze the several small, less informative nuclear magnetic dipole-dipole and spin-rotation interactions that broadened or slightly split some of the low  $J$  transitions.

The spectra observed and analyzed in our study are summarized in Tables I-III. The spectra and assignments are similar to those reported for the CF<sub>3</sub>H-NH<sub>3</sub> symmetric top dimer by Fraser *et al.*,<sup>23</sup> except that SiF<sub>4</sub>-NH<sub>3</sub> might be expected to have a small barrier to internal rotation. Determination of the barrier requires observation of higher internal rotation states than are accessible at the 3 K beam temperature of our spectrometer. Table I gives the <sup>14</sup>N hfs of the most abundant species, <sup>28</sup>SiF<sub>4</sub>-NH<sub>3</sub> for the three lowest  $\Delta J=1$  transitions, in the  $m=0$  and  $\pm 1$  internal rotation states of the NH<sub>3</sub>.<sup>23</sup> The hfs was fitted by standard methods in the  $I+J=F$  basis.<sup>24</sup> It was useful in confirming that the  $J=1\rightarrow 2$  and  $2\rightarrow 3$  transitions are for  $K=0$ . The <sup>14</sup>N hfs for the  $J=0\rightarrow 1$  transitions of the  $m=0$  state was observed in the <sup>29</sup>Si and <sup>30</sup>Si species at natural abundance. The  $\chi_{aa}$  (<sup>14</sup>N) and rotational constants determined by the fitting are summarized in Table III.

<sup>15</sup>NH<sub>3</sub> was used to avoid the <sup>14</sup>N hfs and obtain more readily a complete set of transition frequencies for the silicon isotopes. The results given in Table II include the three lowest  $\Delta J=1$  transitions for both the  $m=0$  and  $\pm 1$  states. The rotational constants  $B_0$  and  $D_J$  found by fitting these data are included in Table III. The results show that the dimer is a symmetric top.

### Structure determination

We next consider the question of internal rotation. For  $K=0$  transitions of a symmetric top with a free internal rotor the spectrum can be fitted to an expression of the type<sup>22</sup>

$$\nu = 2(J+1)[B_0 + Gm^2 - 2D_J(J+1)^2], \quad (1)$$

where  $G$  is a constant describing the coupling between internal rotation and the molecular vibrations. The term in  $G$  was ignored in fitting the  $m = \pm 1$  data of Tables I and II. However,  $G$  is readily found to be  $-39(3)$  kHz from the differences between the frequencies observed for the  $m = \pm 1$  and  $m=0$  states. Isotopic substitution has no visible effect upon the value of  $G$  nor do there appear to be any systematic discrepancies in its fit of the differences. This is consistent with a free rotor, but perturbations by a small barrier may require observation of higher  $m$  and  $J$  states for detection. It may be relevant that the quality of the fit for the  $m = \pm 1$  state (Table I) is much poorer than that for  $m=0$ . In any case,

TABLE I. The <sup>14</sup>N hfs observed and fitted<sup>a</sup> for the  $m = 0$  and  $\pm 1$  internal rotation states of the <sup>28</sup>SiF<sub>4</sub>-NH<sub>3</sub> dimer.

$F \rightarrow F'$	$K = 0, m = 0$ (MHz)	Obs-calc (kHz)	$K = 0, m = \pm 1$ (MHz)	Obs-calc (kHz)
$J = 0 \rightarrow 1$				
1 → 1	5 004.2641	-0.4	5 004.1945	2.7
1 → 2	5 005.0924	-1.5	5 005.0312	10.1
1 → 0	5 006.3423	-4.2	5 006.2622	3.0
$J = 1 \rightarrow 2$				
2 → 2	10 009.0647	0.0	10 008.9153	-0.4
0 → 1	10 009.2038	0.8	<sup>b</sup>	
1 → 2	10 009.8982	4.1	10 009.7436	-1.4
2 → 3	10 009.9522	-1.2	10 009.8003	-4.0
1 → 1	10 011.2710	-5.5	10 011.1252	-2.1
$J = 2 \rightarrow 3$				
3 → 3	15 013.9060	-3.5	...	...
1 → 2	15 014.6626	2.7	15 014.4291	1.5
2 → 3	15 014.7990	0.9	15 014.5582	-7.7
3 → 4	15 014.8317	0.7	15 014.6009	2.1
2 → 2	15 016.0420	-0.3	15 015.8161	6.1

<sup>a</sup>The hfs was fitted simultaneously for the three transitions of each  $m$  state.<sup>b</sup>Not well resolved.TABLE II. Transition frequencies observed and fitted<sup>a</sup> for the  $m = 0$  and  $\pm 1$  internal rotation states of the <sup>15</sup>N isotopic species of the SiF<sub>4</sub>-NH<sub>3</sub> dimer.

$J \rightarrow J'$	$K = 0, m = 0$ (MHz)	Obs-calc (kHz)	$K = 0, m = \pm 1$ (MHz)	Obs-calc (kHz)
<sup>28</sup> SiF <sub>4</sub> - <sup>15</sup> NH <sub>3</sub>				
0 → 1	4 912.8922	-1.4	4 912.8022	-7.6
1 → 2	9 825.7697	1.1	9 825.6135	6.0
2 → 3	14 738.6062	0.3	14 738.3795	1.5
<sup>29</sup> SiF <sub>4</sub> - <sup>15</sup> NH <sub>3</sub>				
0 → 1	4 912.2907	0.8	4 912.2211	5.6
1 → 2	9 824.5603	-0.6	9 824.4065	-4.5
2 → 3	14 736.7945	0.2	14 736.5673	-1.1
<sup>30</sup> SiF <sub>4</sub> - <sup>15</sup> NH <sub>3</sub>				
0 → 1	4 911.6904	-2.5	4 911.6018	-6.4
1 → 2	9 823.3691	2.0	9 823.2104	5.1
2 → 3	14 735.0035	0.5	14 734.7788	1.3

<sup>a</sup>The results of the fit are included in Table III.TABLE III. Spectroscopic properties for the  $m = 0$  and  $\pm 1$  internal rotation states of SiF<sub>4</sub>-NH<sub>3</sub> determined with several isotopic species from their rotational spectra.<sup>a</sup>

Isotopic species	$m = 0$			$m = \pm 1$		
	$B_0$	$D_J$	$\chi_{aa}$	$B_0$	$D_J$	$\chi_{aa}$
<sup>28</sup> SiF <sub>4</sub> - <sup>14</sup> NH <sub>3</sub>	2502.479(1)	0.72(3)	-2.765(3)	2502.443(1)	0.86(7)	-2.764(6)
<sup>29</sup> SiF <sub>4</sub> - <sup>14</sup> NH <sub>3</sub>	2502.229(1)	<sup>b</sup>	-2.768(1)			
<sup>30</sup> SiF <sub>4</sub> - <sup>14</sup> NH <sub>3</sub>	2501.984(2)	<sup>b</sup>	-2.763(10)			
<sup>28</sup> SiF <sub>4</sub> - <sup>15</sup> NH <sub>3</sub>	2456.449(1)	0.79(5)	...	2456.406(4)	0.5(2)	...
<sup>29</sup> SiF <sub>4</sub> - <sup>15</sup> NH <sub>3</sub>	2456.147(1)	0.78(2)	...	2456.109(3)	0.8(2)	...
<sup>30</sup> SiF <sub>4</sub> - <sup>15</sup> NH <sub>3</sub>	2455.848(1)	0.77(7)	...	2455.805(3)	0.5(2)	...

<sup>a</sup>Values given in parentheses are one standard deviation of the fit.<sup>b</sup>Assumed to be 0.7 kHz in order to obtain a value for  $B_0$  from the  $J = 0 \rightarrow 1$  line center.

the applicability of Eq. (1) to our data confirms the assignment of the spectra which was difficult because of the congestion. Also, it validates our choice of the  $B_0$ 's for the  $m = 0$  state in the structural analysis.

Assignment of the spectrum as a symmetric top restricts severely the range of possible structures. However, the strong bonding in the SiF<sub>4</sub>-NH<sub>3</sub> adduct deforms the monomers and increases the structural features of interest. The *ab initio* calculations<sup>3</sup> predict a flattened SiF<sub>4</sub> with longer Si-F bonds,  $\angle F_{eq}-Si-F_{ax} = 118.2^\circ$  instead of tetrahedral and  $r(Si-F) = 1.612$  and  $1.608$  Å for axial and equatorial fluorines vs  $1.5535$  Å in free SiF<sub>4</sub>.<sup>25</sup> Perturbation of the NH<sub>3</sub> is minor and has negligible effect upon the results of our analysis.

Putting aside for now the structure of SiF<sub>4</sub>, the moment of inertia  $\langle I_{bb} \rangle$  observed for the dimer is given in terms of monomer properties and the coordinates pictured in Fig. 1 by the following expression:<sup>23</sup>

$$\langle I_{bb} \rangle = \mu_d R^2 + I_{bb}(SiF_4) + \frac{I_{bb}(NH_3)}{2} \langle 1 + \cos^2 \theta \rangle + \frac{I_{cc}(NH_3)}{2} \langle \sin^2 \theta \rangle, \quad (2)$$

where  $\mu_d$  is the reduced mass of the dimer treated as diatomic and  $R$  is the distance along the symmetry axis between the centers of mass of the two monomers. The  $I_{bb}$  and  $I_{cc}$  are the moments appropriate for the subunits of the dimer. The angular terms describe the effects of bending vibrations of the monomers. They are small for NH<sub>3</sub> and negligible for SiF<sub>4</sub>, because of its near  $T_d$  symmetry.

We use a substitution method to explore the deformation of the SiF<sub>4</sub>. Of necessity, the Si and N atoms lie on the threefold  $a$  axis where their  $a$  coordinates are readily obtained from the isotopic  $B_0$ 's in Table III with the usual relation (Ref. 24)  $|a_i| = (\Delta I / \mu_s)^{1/2}$ , using <sup>28</sup>SiF<sub>4</sub>-<sup>15</sup>NH<sub>3</sub> as the parent species. If the SiF<sub>4</sub> were not deformed, the Si would be at its c.m. (center of mass). Inspection of Fig. 1 shows that in this event

$$R = a(Si) + a(N) + \Delta r^0(NH_3) \langle \cos \theta \rangle. \quad (3)$$

The last term is the distance between the N and the c.m. (NH<sub>3</sub>) projected onto the  $a$  axis by bending vibrations of the NH<sub>3</sub>.

The average bending angle can be estimated with the relation<sup>24</sup>

$$\chi_{aa} = (\chi_0/2) \langle 3 \cos^2 \theta - 1 \rangle \quad (4)$$

from the  $\chi_{aa}$  (<sup>14</sup>N) value of  $-2.765$  MHz found for the dimer. Here  $\chi_0$  is the coupling constant of  $-4.090$  MHz (Ref. 26) found in free NH<sub>3</sub> and assumed to be unaffected by dimer formation. On this basis we find  $\theta$  to be  $27.7^\circ$  and  $\Delta r^0(^{15}NH_3) \langle \cos \theta \rangle$  to be  $0.0555$  Å.

For the Si and N substitution positions the 28-15 species was used as the parent. It was paired with 29-15 and 30-15 to obtain  $-0.1599(2)$  Å for  $a(Si)$  and with 28-14 to find  $1.9402$  Å for  $a(N)$ . The  $2.10$  Å separation of Si and N confirms the orientations assumed for the two monomers in Fig. 1. The results also enable us to check on the position of c.m. (SiF<sub>4</sub>). The distance of the <sup>15</sup>NH<sub>3</sub> c.m. from the dimer c.m.

is  $a(N) + \Delta r^0(^{15}NH_3) \langle \cos \theta \rangle$ , which we now know is  $1.9957$  Å. By applying the first moment condition to this result we find that the c.m. of the SiF<sub>4</sub> is  $0.3460$  Å from the dimer c.m. Thus the deformation of the SiF<sub>4</sub> moves its c.m.  $0.1861$  Å away from the Si. A test calculation shows that the *ab initio* structure for <sup>28</sup>SiF<sub>4</sub> has its c.m. displaced along the axial bond by  $0.1764$  Å which agrees very well with the distortion found. This analysis also gives a value for  $R$  in the 28-15 isotopic species of  $1.9957 + 0.3460$  Å, which may be checked by applying Eq. (2) to the  $B_0$  observed for this species. In the check we use  $I_{bb}(^{28}SiF_4) = 121.140$  amu Å<sup>2</sup>, calculated for the *ab initio* structure,<sup>25</sup> while the values for  $I_{gg}(^{15}NH_3)$  were obtained from the reported structure.<sup>26</sup>

The check gives  $R$  to be  $2.322$  Å which is visibly smaller than the substitution-based value of  $2.342$  Å. However, the Si is close to the c.m. of the dimer, where the substitution method is prone to error and the difference is modest compared with the  $0.18$  Å displacement in the c.m. of SiF<sub>4</sub> in the dimer. Certainly, the results demonstrate that the SiF<sub>4</sub> is compressed substantially by its interaction with the NH<sub>3</sub> and that the *ab initio* calculation predicts that distortion quite accurately.

The isotopic dependence of  $B_0$  in Table III exhibits some interesting features. The  $B_0$ 's for the three Si isotopomers with <sup>14</sup>N are very closely spaced at 2502.0 to 2502.5 MHz while those with <sup>15</sup>N are 46 MHz smaller, at 2455.8 to 2456.4 MHz. This difference reflects of course the fact that the Si is almost at the c.m. of the dimer while the N is at the low-mass end. In spite of the small Si isotope effects they do confirm the *ab initio* structure. The  $B_0$ 's for the <sup>15</sup>N species are more accurate than those for 29-14 and 30-14 so we use only the Si-15 species in the analysis. The observed  $B_0$ 's were fitted to Eq. (2) by calculating  $I(^{15}NH_3)$  from the available data<sup>26</sup> and by using the *ab initio* structure of SiF<sub>4</sub> in the dimer to determine the  $I_{bb}$  for each isotopic species;  $R$  was the adjustable parameter. The results are summarized in Table IV. It is seen that there is a systematic decrease in  $R$  of  $0.0017$  Å on going from <sup>28</sup>Si to <sup>29</sup>Si to <sup>30</sup>Si. One would not expect the isotopic substitution to affect the actual intermonomer distance appreciably so the decrease should reflect an

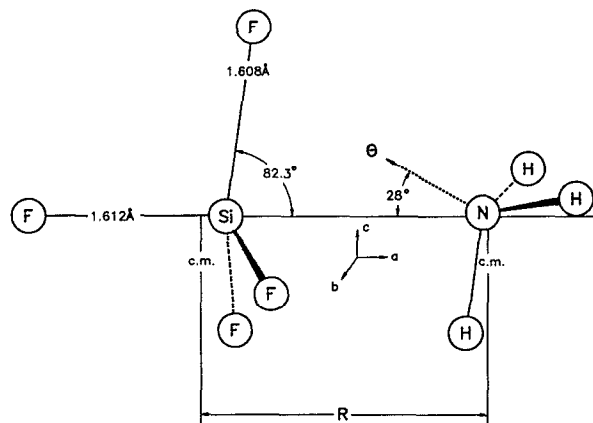


FIG. 1. Geometry of the SiF<sub>4</sub>-NH<sub>3</sub> dimer and coordinates used to describe its structure. Interatomic dimensions are to scale. The distortion given for SiF<sub>4</sub> is that predicted by the *ab initio* calculation (Ref. 3).

TABLE IV. Dependence of  $R$  on Si isotopic substitution, determined by fitting  $B_0$  with Eq. (2), compared with the isotopic shift in SiF<sub>4</sub> c.m. to Si distance  $r$ .

Species	$\langle I_{bb} \rangle$ (amu Å <sup>2</sup> )	$I_{bb}$ (SiF <sub>4</sub> ) (amu Å <sup>2</sup> )	$I(^{15}\text{NH}_3)^a$ (amu Å <sup>2</sup> )	$R$ (Å)	$\Delta R$ (Å)	$r(\text{Si-c.m.})$ (Å)	$\Delta r$ (Å)
28-15	205.736	121.140	1.806	2.3216	...	0.1765	...
29-15	205.761	121.171	1.806	2.3199	0.0017	0.1748	0.0017
30-15	205.786	121.201	1.806	2.3182	0.0017	0.1731	0.0017

<sup>a</sup>Based on values of 1.699 and 2.685 amu Å<sup>2</sup> for  $I_{bb}$  and  $I_{cc}$  of <sup>15</sup>NH<sub>3</sub>, with a  $\theta$  of 27.7°.

isotopic shift in the SiF<sub>4</sub> c.m. Indeed, this proves to be the case. For the *ab initio* structure one finds the distance  $r$  between the Si and the SiF<sub>4</sub> c.m. to be  $0.9658 m_F/M$  Å where  $M$  is the molecular weight. Increasing the silicon mass moves the predicted c.m. closer to the Si, by 0.0017 Å for each increase in Si mass, as summarized in Table IV. The effect is small but the close agreement between observed and predicted shifts is strong support of the deformation predicted by the *ab initio* calculation.

### Dipole moment

The dipole moment  $\mu_a$  of the <sup>28</sup>SiF<sub>4</sub>-<sup>15</sup>NH<sub>3</sub> dimer was determined with the Stark assembly described previously.<sup>27</sup> The assembly was calibrated by means of the  $\Delta M = 0$  Stark component for the  $J = 0 \rightarrow 1$  transition of OCS at 12 162.979 MHz.<sup>28</sup> It was used to measure the second order Stark effect up to 175 V/cm of the  $M = 0$  and  $\pm 1$  components for the  $J = 2 \rightarrow 3$  transitions of the  $K = 0$ ,  $m = 0$  and  $\pm 1$  states of the dimer. The results are summarized in Table V. A few measurements were made of the  $\Delta M = \pm 2$  components (not given). Values of 5.612(10) and 5.626(5) D, respectively, were found for  $\mu_a$ . The second order dependence confirms that the species observed is a symmetric top.<sup>24</sup>

The measurements were made with the molecular beam axis coincident with the axis of the Fabry-Perot cavity. In

this configuration the beam traverses the entire length of the cavity and the effective electric field of the Stark assembly is slightly dependent on the distance from the nozzle at which the microwave pulse is applied. Therefore, the same time sequence was used in calibration and measurement runs.

### DISCUSSION

The structural information found for the SiF<sub>4</sub>-NH<sub>3</sub> dimer is limited somewhat by its being a symmetric top with no fluorine isotopes. Nonetheless, the basic features are well established. The overall geometry is that given in Fig. 1. Moreover, dimer formation compresses the equatorial fluorines substantially. The isotopic dependence of the rotational constants is in excellent agreement with the SiF<sub>4</sub> deformation predicted by *ab initio* methods. In particular, the altitude of the SiF<sub>3</sub> (eq) pyramid is squashed from 0.518 Å in free SiF<sub>4</sub> to 0.215 Å in the dimer. However, we do not have independent values for  $r(\text{F}_{ax})$  or for  $\angle \text{F}_{eq}-\text{Si}-\text{F}_{eq}$ .

An accurate Si to N distance can be determined from  $R$ , 2.3216 Å, in Table IV by subtracting the c.m. (SiF<sub>4</sub>) to Si distance ( $r$ ) of 0.1765 Å and the N to c.m. (<sup>15</sup>NH<sub>3</sub>) distance of 0.0555 Å. The result of 2.090 Å is appreciably less, 0.054 Å, than the *ab initio* value.<sup>3</sup> This is typical of such calculations.<sup>29</sup>

TABLE V. Frequencies (MHz) observed for the  $J = 2 \rightarrow 3$ ,  $K = 0$ ,  $m = 0$  and  $\pm 1$  transitions of <sup>28</sup>SiF<sub>4</sub>-<sup>15</sup>NH<sub>3</sub> at various electric field strengths, and the dipole moments determined therefrom.

$E$ (V/cm)	$m = 0$		$m \pm 1$	
	$M = 0$	$M = \pm 1$	$M = 0$	$M = \pm 1$
0.0	14 738.6062	14 738.6062	14 738.3795	14 738.3795
29.12	8.5792	8.5961	8.3434	
29.63	8.5679	8.5964	8.3407	
32.26		8.5937	8.3353	8.3650
34.42		8.5925		8.3626
35.66		8.5915		8.3616
48.08		8.5801		8.3490
59.49		8.5651	8.2302	7.3348
70.67		8.5483		8.3184
75.31		8.5400	8.1445	8.3101
93.73		8.5028		8.2741
102.30		8.4836	7.9425	8.2541
130.39		8.4082		8.1783
173.97		8.2538		8.0259
$\mu$ (Debye)		5.612(10)		5.626(5)

There are some interesting questions about the mobility of the monomers in the dimer. We have seen, for example, that the barrier to internal rotation is small or nonexistent. This is in spite of a separation along the *a* axis between F<sub>eq</sub> and H of only 2.24 Å and a relatively large interaction energy,  $\Delta E = 7.6$  kcal/mol (Ref. 3), between the monomers. Moreover, the bending amplitude of the NH<sub>3</sub> is exceptionally high, 27.7°, in light of the small *D<sub>J</sub>* of 0.78 kHz. Some of this is undoubtedly due to charge redistribution effects which change  $\chi_0$  (NH<sub>3</sub>).<sup>30,31</sup> It also seems possible that the deformation of the SiF<sub>4</sub> leads to a smoother potential surface between the monomers. At least the dimensions shown in Fig. 1 give a nice catcher's "fist-in-glove" structure.

The measured dipole moment  $\mu_a$  of 5.612 D for the *m* = 0 state of the dimer is much larger than the sum of the free monomer moments. SiF<sub>4</sub> is nonpolar so the sum is simply 1.468 D, the value for free NH<sub>3</sub>.<sup>32</sup> The increase upon dimer formation of 4.144 D is certainly one of the largest on record. In principle, it could result from charge rearrangement, be a consequence of the structural deformation, or both. Recent work<sup>6,33</sup> on charge partitioning in SiH<sub>3</sub>F led us to believe that the Si-F bond is probably very polar. This, along with the dramatic geometric rearrangement of the SiF<sub>4</sub> upon formation of SiF<sub>4</sub>-NH<sub>3</sub> led us to explore the effect upon the dipole moment of the deformation.

We assumed an oversimplified point charge model with *no* charge transfer and *no* polarization contributions to the 4.14 D increase determined. That is, the model ascribes all of the 4.14 D increase to the distorted geometry in which the Si-F<sub>eq</sub> bonds are nearly perpendicular to the *a* axis and therefore contribute little to  $\mu_a$ . By assuming the Si-F<sub>ax</sub> and Si-F<sub>eq</sub> bonds to be equivalent we can determine the point charges on the Si and F's which fit the dipole moment of the deformed SiF<sub>4</sub>. This gives -0.88 *e* for the fluorines and +3.52 *e* for the silicon.

Soon after measurement of the SiF<sub>4</sub>-NH<sub>3</sub> dipole moment and application of the point charge model just described, Keith and Bader<sup>31</sup> made direct calculations of the partitioned charges in SiF<sub>4</sub>-NH<sub>3</sub> dimer as well as in the free NH<sub>3</sub> and SiF<sub>4</sub> monomers. The Bader method is sounder than the Mulliken population analysis for partitioning charge to nuclei.<sup>6</sup> Also, it allows assignment of the charge transfer, polarization, and geometric changes in the SiF<sub>4</sub> dipole moment increase.<sup>8,34,35</sup>

Keith and Bader determine partial charges on the F and Si atoms in SiF<sub>4</sub> to be -0.85 and +3.4 with slight (about 0.02) changes in the F charge upon dimer formation. The agreement with our point charge model is partly fortuitous. There are small contributions from polarization and charge transfer to the calculated dipole moment increase, which they determine to be 4.15 D in essentially exact agreement with experiment. However, by far the largest contribution (89%) is from the unbalanced Si-F bond moments caused by the displacement of the three equatorial F atoms. Thereby, the measurement of the dipole moment of SiF<sub>4</sub>-NH<sub>3</sub> has

allowed us to reveal the extraordinary ionicity of the Si-F bond in SiF<sub>4</sub>. Also it provides, as far as we are aware, the first experimental verification of the Bader charge partitioning scheme.

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