

no "unusual" bonded distances.

The calculations, which were of the extended Hückel type, have employed the ICON program written by the Hoffmann group.⁷⁴ For calculations on systems such as those of Figure

(73) Note that this distortion is another failure of the second-order Jahn-Teller approach to A_2X_2 geometries: Pearson, R. G. *J. Chem. Phys.* **1970**, *52*, 2167. Since the HOMO and LUMO are of a and b symmetry species, the second-order Jahn-Teller transition should be of b symmetry. It is however an a species distortion (the torsion of N_2F_2) that sends the skew (C_2) structure to either cis or trans planar forms, a point not mentioned in Pearson's paper.

6 and in 19-21, all chemically inequivalent distances were kept equal so as not to bias the results of the population analysis. Standard AX and AA distances were used for molecules such as SF_2 , OF_2 , etc., and the same AX distances were also used therefore for the O_2F_2 , S_2F_2 , etc. molecules in Figure 6. Standard orbital parameters⁵ were used.

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Ab Initio Studies on the Ground-State Potential Surface and Vibrational Spectra of NSF and SNF

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Received January 13, 1984

Theoretical vibrational spectra were calculated for NSF and SNF by the use of the 6-31G* basis. They are sufficiently different to be useful in the identification of the yet unknown SNF. Geometry optimizations were also carried out at the 6-31G*/MP2 level on these two minima and on the transition state connecting them. The activation energy for the conversion of SNF to NSF is predicted to be high enough to allow isolation of SNF at room temperature.

While thiazyl fluoride (NSF)¹⁻⁵ has been known for a number of years, its isomer SNF is unknown. Previous theoretical studies^{6,7} have indicated that SNF does represent a second minimum on the (N, S, F) potential surface. Quite recently the overall potential surface, including the saddle point connecting the two isomers, has been examined at the Hartree-Fock level.⁸ Here we shall describe Hartree-Fock plus correlation (MP2) calculations of the two minima and the transition structure. Theoretical vibrational spectra of the two minima are also presented to aid in the eventual identification of the isomer SNF.

Computational Details

Molecular Orbital Calculations. All calculations described here were done with the standard 6-31G* basis set developed by Pople and his co-workers.⁹ Electron correlation was included by second-order perturbation theory with the Møller-Plesset (MP2) partitioning of the Hamiltonian.¹⁰ The SCF calculations were carried out either with a modified version¹¹ of HONDO 5,¹²⁻¹⁵ in which the BMAT link of Pulay's program TEXAS¹⁶⁻¹⁸ is incorporated for geometry optimization, or with GAUSSIAN 80.¹⁹ MP2 calculations were performed by a program²⁰ written to be used with HONDO 5.

Geometry Optimization. For NSF at the SCF level a set of force constants obtained from the literature^{21,22} was used with the modified HONDO 5.¹¹ The force constants were not kept constant as in the original force method,^{17,18} but they were modified after three cycles because of slow convergence. This was done by using gradients from the three cycles in conjunction with an independent BMAT¹⁶⁻¹⁸ program. An iterative variation of the diagonal force constants was carried out until the three predicted geometries from the three gradients were consistent. The geometry thus obtained from the third-cycle gradient was then used in a fourth energy and gradient calculation, which was taken as the final point since the largest component of the Cartesian gradient was less than 0.001 hartree/bohr. For SNF the optimization

Table I. Calculated Quadratic Force Constants for NSF and SNF^a

const	NSF		SNF	
	6-31G*	6-31G*/MP2	6-31G*	6-31G*/MP2
F_{NS}	12.237	15.886	9.220	6.485
F_{SF}	4.625	3.430		
F_{NF}			5.812	3.835
F_{α}	1.465	1.039	2.035	1.774
$F_{\alpha,NS}$	0.519	0.212	0.505	0.516
$F_{\alpha,SF}$	0.046	-0.206		
$F_{\alpha,NF}$			0.782	0.490
$F_{NS,SF}$	0.630	0.219		
$F_{NS,NF}$			1.294	0.902

^a Stretching force constants are in $\text{mdyn } \text{Å}^{-1}$, bending force constants in $\text{mdyn } \text{Å} \text{ rad}^{-2}$, and stretching-bending interactions in $\text{mdyn } \text{rad}^{-1}$.

procedure in GAUSSIAN 80 was used since no experimental force constants were available.

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Table II. Geometries, Energies, and Dipole Moments^a

	NSF				saddle point		SNF		
	DZ + d ^b	6-31G*	6-31G*/MP2	exptl ^c	DZ + d ^b	6-31G*/MP2	DZ + d ^b	6-31G*	6-31G*/MP2
R_{NS}	1.432	1.432	1.436	1.446	1.413	1.51	1.528	1.528	1.580
R_{SF}	1.634	1.615	1.665	1.646	2.318	2.32	2.405	2.400	2.469
R_{NF}	2.558	2.557	2.651	2.637	2.063	2.06	1.347	1.351	1.432
μ	2.31	2.15		1.902	6.97		1.67	1.40	
E	-551.34944	-551.30065	-551.71261		-551.22992	-551.61769	-551.30189	-551.25064	-551.67090

^a Bond distances in angstroms, dipole moments in debyes, and energies in hartrees. ^b (12,9,2/9,5,1); see ref 8. ^c Structure values from ref 2; dipole moment from ref 3 and 27.

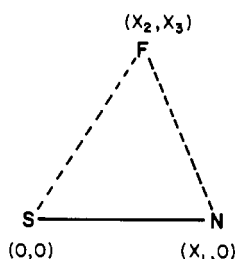


Figure 1. Cartesian coordinates (X_1 , X_2 , and X_3) used in the search for the transition state. Sulfur was held fixed at the origin, nitrogen was varied in the X direction (X_1), and fluorine was varied in the X (X_2) and Y (X_3) directions.

For NSF and SNF complete geometry optimizations were carried out at the 6-31G*/MP2 level by varying the three internal coordinates point by point. The transition state was located in the following manner. Let X_1 , X_2 , and X_3 be the Cartesian coordinates indicated in Figure 1, and let X_1° , X_2° , and X_3° be their values at some point where the energy is V° . It was assumed that near this point changes in the potential can be approximated by

$$\Delta V = V - V^\circ = a_1(\Delta X_1)^2 + a_2(\Delta X_2)^2 + a_3(\Delta X_3)^2 + a_{12}\Delta X_1\Delta X_2 + a_{13}\Delta X_1\Delta X_3 + a_{23}\Delta X_2\Delta X_3 + b_1\Delta X_1 + b_2\Delta X_2 + b_3\Delta X_3 \quad (1)$$

where $\Delta X_i = X_i - X_i^\circ$. The initial point chosen was the SCF geometry found by Gleiter.⁸ The nine parameters in eq 1 were determined by computing ΔV with single positive and negative distortions of the three X 's and with combinations of (ΔX_1 , ΔX_2 ; ΔX_1 , ΔX_3 ; ΔX_2 , ΔX_3). Then, setting the gradient of eq 1 equal to zero with these nine parameters gives three linear equations for ΔX_1 , ΔX_2 , and ΔX_3 at a stationary point of eq 1. These form the second approximation to the transition state, and the cycle was repeated there. Several cycles were required before the saddle point was found to a reasonable degree of accuracy. As the saddle point was approached, the values of the b 's approached zero and diagonalization of the a 's gave an approximation to the normal-mode force constants. At the final geometry one of these was found to be negative as is expected for a transition state.

Vibrational Calculations. Force constants, vibrational frequencies, and IR intensities were determined as described previously.²³ In these determinations 6-31G* and 6-31G*/MP2 wave functions were employed, and the corresponding optimized geometries were used in the vibrational analysis. For both NSF and SNF the two bond distances and the angle made by the two bonds (α) were taken as the internal

Table III. Relative Energies^a

	$E^\ddagger - E_{NSF}$	$E^\ddagger - E_{SNF}$	$E_{SNF} - E_{NSF}$
4-31G ^b	59.9	56.5	3.3
(12,9,2/9,5,1) ^b	75.0	45.2	29.8
6-31G*			31.4
4-31G/MP2 ^b	14.3	20.0	-5.7
(12,9,2/9,5,1) + estd correln energy ^b	29.4	8.6	20.8
6-31G*/MP2	59.6	33.4	26.2

^a E^\ddagger is the energy of the transition state. All energies are in kcal/mol. See footnote 26. ^b Reference 8.

Table IV. Vibrational Frequencies and Intensities of NSF and SNF^a

NSF			SNF	
6-31G*	6-31G*/MP2	exptl ^b	6-31G*	6-31G*/MP2
451 (906)	367	366	543 (29)	478
814 (10 492)	716	640	1044 (10 175)	870
1448 (794)	1662	1372	1267 (5196)	1049

^a Frequencies are in cm^{-1} . Intensities are shown in parentheses with units of 10^3 cm mol^{-1} . ^b Reference 24.

coordinates. The resulting force constants are given in Table I.

Results and Discussion

In Table II are listed the optimized geometries found for the two minima and the saddle point by us and by Seeger, Seeger, Bartetzko, and Gleiter.⁸ For NSF and SNF our SCF results (6-31G*) compare favorably with those obtained from the somewhat larger basis in ref 8. Inclusion of correlation (MP2) gives the expected increase in bond distances over the SCF results for NSF and SNF, but interestingly for the saddle point the only significant change in geometry at the MP2 level was a lengthening in the NS bond distance. On the other hand, the relative energies of the three species in Table III are quite dependent upon basis set and correlation effects. As concluded previously,⁸ it is seen from Table III that inclusion of polarization functions has a dramatic effect on the relative SCF energies of NSF and SNF. Their inclusion changes this difference in energy from about 3 to 30 kcal/mol. Correlation (MP2) with the 6-31G* basis modifies this difference by only a modest amount (~ 5 kcal/mol). One sees a slightly larger effect on going from 4-31G to 4-31G/MP2 (9 kcal/mol), but note that with 4-31G/MP2 SNF is predicted to be more stable than NSF.

The first two columns in Table III represent the activation energies for isomerization from NSF to SNF and from SNF to NSF, respectively. Seeger, Seeger, Bartetzko, and Gleiter⁸ found very large activation energies at the SCF level even with polarization functions. This indicates that both isomers should be easily isolable as distinct species at room temperature. On the other hand, when they made an estimate of the correlation energies of their (12,9,2/9,5,1) wave functions on the basis of their 4-31G/MP2 results, a very different conclusion was

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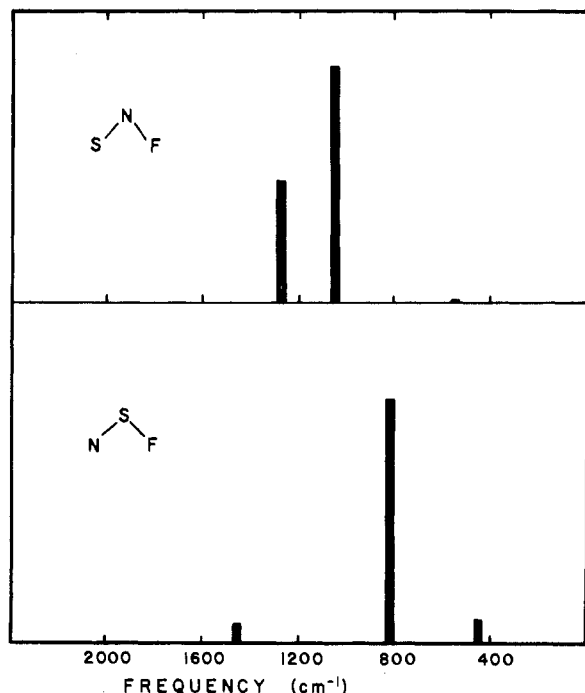


Figure 2. Computed IR spectra (6-31G*) of NSF and SNF. Intensities are relative to the strongest band in NSF at 814 cm^{-1} .

reached. Namely, the conversion of SNF to NSF was estimated to have an activation barrier of only 8.6 kcal/mol. This would preclude the isolation of SNF at room temperature. However, our results with correlation (6-31G*/MP2) give an activation energy of 33.4 kcal/mol for this isomerization, which suggests that SNF should be isolable at or near room temperature.

In Table IV the IR frequencies for both NSF and SNF are given along with predicted intensities. A comparison of the 6-31G* calculated frequencies with experimental frequencies²⁴ for NSF indicates quite reasonable agreement, although all frequencies are calculated to be too high as we have earlier found²⁵ with the 6-31G* basis set. No quantitative data are available for the intensities of the IR bands of NSF. Inclusion of correlation (6-31G*/MP2) is seen to improve greatly the agreement between theory and experiment for two of the three bands. However, for the N-S stretch agreement is worse at this level, with this band calculated to be at even higher frequency than with the 6-31G* wave function. We have noted similar erratic behavior of the calculated frequency of the C-S stretch in thirene as the basis set is changed.²⁸ On the other hand, for SNF we find the anticipated decrease in frequencies on going from the 6-31G* to the 6-31G*/MP2 basis set. The 6-31G* spectra of NSF and SNF are shown in Figure 2, and it is seen that they are quite different.

In conclusion, it is found that although SNF has a higher energy minimum than NSF, the isomerization from SNF to NSF has a sufficiently high activation energy to make SNF experimentally accessible and that the IR spectra of the two are sufficiently different to allow easy identification of the yet unknown SNF.

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Desolvation Method for Assessment of Crystallization Energies and Ion Crowding in Rare-Earth Perchlorates, Chlorides, and Nitrates

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Received December 5, 1983

Gibbs energy changes on removal of solvent water to crystallize rare-earth perchlorates, chlorides, and nitrates from saturated solutions have been computed from activity data in the literature. These values are combined with heat of dilution data to give second-law entropy changes. Perchlorates and chlorides require about the same Gibbs energy change for crystal formation, although the saturated solution compositions are considerably different. Nitrates require about half of the Gibbs energy change required for perchlorates and chlorides. The work requirement for crystallization of $[\text{Pr}_2\text{Cl}_2(\text{H}_2\text{O})_{14}]\text{Cl}_4$ is 500 cal mol^{-1} less than for $[\text{NdCl}_2(\text{H}_2\text{O})_6]_2\text{Cl}_2$. Exothermic heat results from crystallization of the former compound, while heat absorption results from crystallization of the latter. All nitrates evolve heat on crystallizing. Second-law values of $T\Delta S$ show that the cation-stabilization energy of $[\text{Pr}_2\text{Cl}_2(\text{H}_2\text{O})_{14}]\text{Cl}_4$ vs. $[\text{PrCl}_2(\text{H}_2\text{O})_6]_2\text{Cl}_2$ is 150 cal mol^{-1} . Entropy changes on crystallization are positive only for perchlorates with atomic numbers larger than that of dysprosium. This behavior is interpreted to indicate a nearly perfect fit of ions and water at dysprosium, with cation crowding at smaller rare-earth atomic numbers and anion crowding at larger atomic numbers. Other ion-crowding effects are discussed. Extrapolations and interpolations for promethium show pivotal behavior that can be resolved when saturated-solution data become available.

Introduction

Many of the reported thermochemical cycles for hydrogen production by water splitting incorporate a step for removal of solvent water to produce a crystalline product for recycle.¹⁻⁷

There is a need for rigorous evaluation of work and heat requirements for crystal formation based on properties of the

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