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Matrix Infrared Spectroscopic and Theoretical of the Difluoroamino Metal Fluoride Molecules: F_2NMF (M = Cu, Ag, Au)

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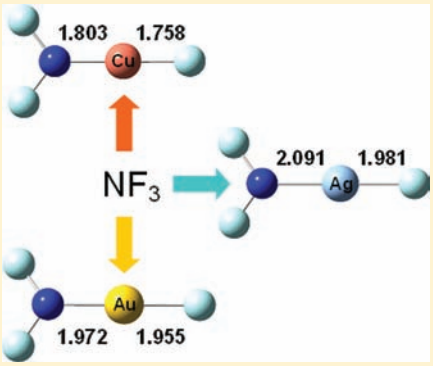
Supporting Information

ABSTRACT: The difluoroamino coinage metal fluoride molecules F_2NMF (M = Cu, Ag, Au) have been made via spontaneous reactions of coinage metals and NF_3 in solid argon and neon matrixes during sample annealing without formation of the $M(NF_3)$ complexes. Comparisons between the matrix infrared spectra and the density functional frequency calculations provide strong support for identification of the F_2NMF molecules, which are found to have doublet ground states with C_{2v} or near C_{2v} geometries. The F_2NCuF molecule can isomerize to the less stable $FNCuF_2$ isomer upon UV−visible irradiation, while no similar reactions were observed for the silver and gold species. The M−N bonds in the F_2NMF molecules are stronger than those in the $FNMF_2$ isomers with the Ag−N bond being longest and weakest in both cases.



INTRODUCTION

The catalytic properties of coinage metals (Cu, Ag, Au) have been well recognized, as evidenced by a number of reactions catalyzed by compounds with coinage metal centers.[1] Although copper catalysts have been known and used for a long time, reactions mediated by silver and gold catalysts have attracted more attention in recent years.[2] In addition to the rich studies on the applications of coinage metal-involved catalysts, studies on the metal-involved intermediates are also important in understanding the detailed catalytic mechanisms. The amido, imido, and nitrido complexes of coinage metals were considered important intermediates in the formation of new C−N bonds.[1,3−6] However, the structural information of these transient species is not well established.[7] While progress has been made in synthetic chemistry,[8−11] reactions of metal atoms with nitrogen-containing species can also serve as an effective method to prepare the molecules with direct metal nitrogen bonds. Ammonia is one of the simplest molecules that can be used in these kinds of reactions. Many examples of ammonia and transition metal as well as uranium and thorium reactions have been reported, in which amido and imido metal complexes were produced and characterized via infrared spectroscopy as well as theoretical calculations.[12−16] As a variation, NF_3 is an even better reactant to start with due to the weak N−F bond, which is only about half as strong as the N−H bond in amonia.[17] Recently, a series of experiments on the reactions of transition metals and NF_3 have been carried out in our lab. For uranium and group VI metal atoms, terminal nitride molecules NMF_3 with M≡N triple bonds were characterized, in which the metal centers are in their highest oxidation state of +VI.[18,19] Reactions with group IV and thorium atoms gave rise to terminal pnictinidene N÷MF_3 molecules with two singly occupied π orbitals as the final products, because of the lack of enough valence electrons to support triple bonds for these tetravalent metal atoms.[20] In addition, fluorine transfer reaction kinetics have also been investigated in the gas phase.[21] In this paper, the reaction products of coinage metals with NF_3 are studied using matrix infrared spectroscopy and density functional calculations, in which the F_2NMF molecules are identified as the major products. The $FNCuF_2$ isomer is also produced upon UV−visible irradiation, while no similar products are observed for silver and gold.

EXPERIMENTAL AND THEORETICAL METHODS

The experimental apparatus and procedure for the preparation of the product molecules in excess argon and neon at 4 K have been described previously.[22] The Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused onto a freshly cleaned copper, silver, or gold target mounted on a rotating rod. Laser-ablated metal atoms were codeposited with 2−4 mmol of argon or neon (Matheson, research) containing 1.0% NF_3 (Air Products) onto a CsI cryogenic window for 60 min (30 min deposition for neon). NF_3 gas was condensed to 77 K using liquid N_2 and evacuated to remove residual N_2 and O_2 before use. FTIR spectra were recorded at 0.5 cm^{-1} resolution on a Nicolet 750 FTIR instrument with a HgCdTe range B detector. Matrix samples were annealed at different temperatures and cooled back to 4 K for spectral acquisition. Selected samples were subjected to broadband photolysis with different glass filters (no filter, λ > 220 nm irradiation; Pyrex filter, λ > 290 nm irradiation; and yellow glass filter, λ > 470 nm irradiation) using a medium-pressure mercury arc street lamp (Philips, 175 W) with the outer globe removed.

Complementary density functional theory (DFT) calculations were performed using the Gaussian 03 program.[23] The hybrid B3LYP density functional was employed in our calculations.[24] The 6-311+G(d) basis set was used for nitrogen, fluorine, and copper

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atoms,[25] and the 28 and 60 electron core SDD pseudopotentials were used for silver and gold.[26] All of the geometrical parameters were fully optimized, and the harmonic vibrational frequencies were obtained analytically at the optimized structures. Transition states for the conversion between F_2NMF and $FNMF_2$ isomers were also optimized using the synchronous transit-guided quasi-Newton method implemented in the Gaussian 03 program.

RESULTS AND DISCUSSION

Experiments with different metals in solid argon revealed that common absorptions due to NF_2 and NF were produced during sample deposition.[27] Further sample annealing increased N_2F_4 bands, while the NF_2 and NF absorptions decreased.[28] UV−visible irradiation (λ > 290 nm) increased both NF and NF_2 bands but more for the former, and the NF_2 band decreased slightly when broad band irradiation (λ > 220 nm) was used. For comparison, the infrared spectra of an NF_3/Ar sample deposited at 4 K without metal followed by 30 K annealing and λ > 220 nm irradiation are shown in Figure S1, traces h−j (Supporting Information), which produce no NF and NF_2 absorptions.

Infrared Spectra. The infrared spectra from the reactions of copper and NF_3 are shown in Figure 1. Absorptions due to

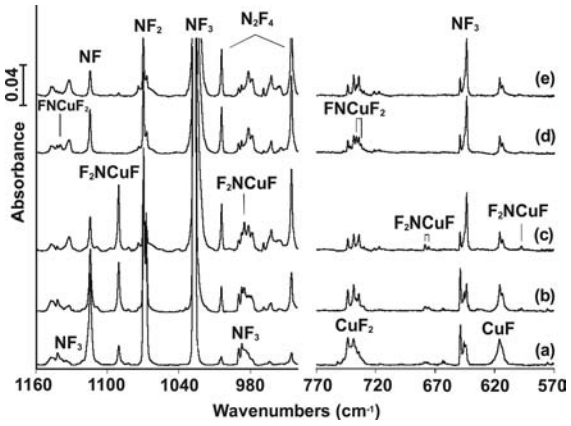

Figure 1. Infrared spectra of laser-ablated Cu atom and NF_3 reaction products in solid argon: (a) Cu + 1.0% NF_3 deposition for 60 min, (b) after annealing to 20 K, (c) after annealing to 35 K, (d) after λ > 290 nm irradiation, and (e) after annealing to 35 K.

CuF and CuF_2 molecules were observed in the spectrum taken right after sample deposition.[29,30] Additionally, a new metal-dependent band at 1090.5 cm^{-1} also appeared (Figure 1, trace a). Subsequent sample annealing results in a substantial growth of this new band. At the same time, another set of absorptions at 985.0, 678.4, 675.5, and 597.5 cm^{-1} also appeared in the infrared spectra, which have identical behavior with the 1090.5 cm^{-1} absorption (Figure 1, traces b and c). UV−visible irradiation with λ > 290 nm filter completely destroyed these newly observed absorptions, during which another group of absorptions at 1139.6, 736.2, and 732.1 cm^{-1} increased. These three bands have never been reported previously (Figure 1, trace d). When the sample was annealed again after UV−visible irradiation, the 1139.6, 736.2, and 732.1 cm^{-1} absorptions sharpened first and then decreased slightly, while the 1090.5 cm^{-1} band slightly increased (Figure 1, trace e, and Figure S1 in the Supporting Information).

Figure 2 shows the infrared spectra from the reactions of laser-ablated silver atoms with NF_3 in solid argon. Similar with the copper experiment, AgF and AgF_2 absorptions were the

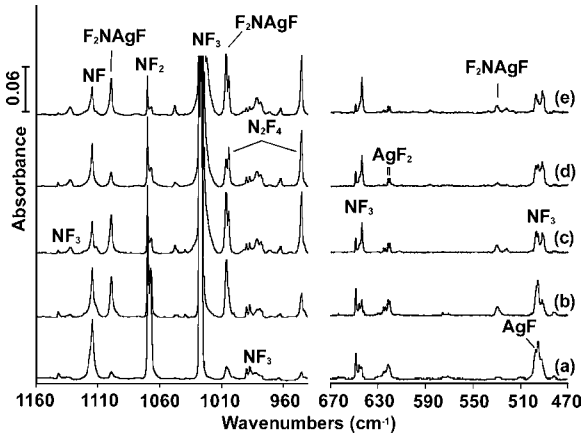

Figure 2. Infrared spectra of laser-ablated Ag atom and NF_3 reaction products in solid argon: (a) Ag + 1.0% NF_3 deposition for 60 min, (b) after annealing to 20 K, (c) after annealing to 35 K, (d) after λ > 220 nm irradiation, and (e) after annealing to 35 K.

major metal-dependent absorptions right after sample deposition (Figure 2, trace a).[30] New product absorptions at 1099.2, 1006.3, and 529.6 cm^{-1} increased markedly when the sample was annealed to 35 K (Figure 2, trace c). These three absorptions decreased more than half upon broad band irradiation (λ > 220 nm) but were produced again during subsequent sample annealing.

Reactions of gold with NF_3 are evidenced by the spectra shown in Figure 3. In addition to the (Ar)AuF and AuF_2

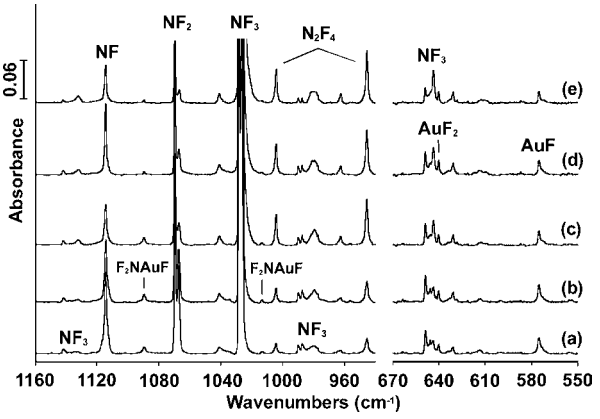

Figure 3. Infrared spectra of laser-ablated Au atom and NF_3 reaction products in solid argon: (a) Au + 1.0% NF_3 deposition for 60 min, (b) after annealing to 20 K, (c) after annealing to 30 K, (d) after λ > 220 nm irradiation, and (e) after annealing to 35 K.

absorptions observed at 575.1 and 640.1 cm^{-1},[30] two new absorptions at 1089.7 and 1013.4 cm^{-1} were observed after sample deposition, and they slightly increased during subsequent annealing. Broad band irradiation (λ > 220 nm) destroyed these two bands, and they were barely recovered when the sample was annealed further.

The copper, silver, gold, and NF_3 reactions were also repeated in a neon matrix. Common absorptions due to NF_2, NF, and NF_3^+ were observed from the infrared spectra taken after sample deposition.[31] As shown in Figure 4, new metal-dependent absorptions were produced with different coinage metals but with lower yields. All of the new bands were completely destroyed when the samples were subject to UV−

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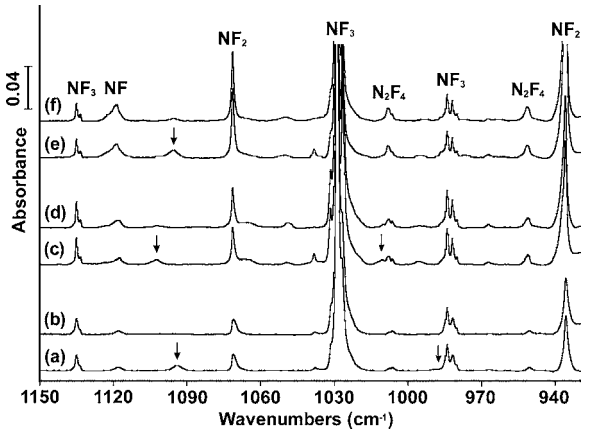

Figure 4. Infrared spectra of laser-ablated coinage metal atom and NF_3 reaction products in solid neon: (a) Cu + 1.0% NF_3 deposition for 30 min followed by annealing to 10 K, (b) after $\lambda > 290$ nm irradiation, (c) Ag + 1.0% NF_3 deposition for 30 min followed by annealing to 10 K, (d) after $\lambda > 220$ nm irradiation, (e) Au + 1.0% NF_3 deposition for 30 min followed by annealing to 8 K, and (f) after $\lambda > 220$ nm irradiation. The arrows indicate the F_2NMF (M = coinage metals) absorptions.

visible irradiation. The product bands observed in argon and neon matrixes are listed in Table 1.

F_2NMF (M = Cu, Ag, Au). The 1090.5, 985.0, 678.4, 675.5, and 597.5 cm^{-1} product absorptions have identical behaviors upon sample annealing and irradiation following the copper reaction in excess argon, suggesting that they are due to different vibrational modes of the same molecule (Figure 1). The two strongest absorptions at 1090.5 and 985.0 cm^{-1} are assigned to N−F stretching modes on the basis of their band positions. Experiments in the neon matrix give two new bands at 1094.3 and 988.2 cm^{-1}. The neon-to-argon matrix shifts are also near shifts (1−4 cm^{-1}) found here for N−F stretching modes in NF_3, NF_2, and NF (Table 1). In the low frequency region, the relative infrared intensities of the 678.4 and 675.5 cm^{-1} absorptions are approximately 2:1, which approach the statistical distribution of natural copper isotopes, indicating the involvement of one copper atom in this vibrational mode. The splitting for these two bands is 2.9 cm^{-1}, slightly larger than that for the diatomic CuF molecule (2.2 cm^{-1}) observed in the same experiment.[30] Hence, the 678.4 and 675.5 cm^{-1} absorptions should arise from $^{63}Cu-F$ and $^{65}Cu-F$ stretching modes coupled with other atoms in such a way that Cu moves antisymmetrically between F and this other atom. Unlike these two bands, the weak band at 597.5 cm^{-1} shows no splitting of copper isotopes, which means the copper atom is not strongly involved in this mode. Because the bending modes of NF_3 are also in the same region, the most probable assignment for this weak new band is an NF_2 bending mode. Accordingly, the newly observed absorptions are assigned to different vibrational modes of the F_2NCuF molecule, which contains the bonds characterized by the above vibrational modes.

In the silver experiment, new product absorptions at 1099.2, 1006.3, and 529.6 cm^{-1} in solid argon are assigned to the F_2NAgF molecule following the copper example (Figure 2). The first two absorptions should be due to the symmetric and antisymmetric F−N−F stretching modes of the NF_2 fragment, while the 529.6 cm^{-1} band arises from the Ag−F stretching mode. Note that the silver isotopic splitting for AgF (497.2 cm^{-1}) is not resolved, the same as the observed Ag−F mode for F_2NAgF. The two N−F modes of the F_2NAgF molecule in solid neon are slightly blue-shifted from their argon counterparts, similar with the case of the copper analog (Figure 4).

Table 1. Observed and Calculated (B3LYP) Vibrational Frequencies for NF_3 and the F_2NMF and $FNMF_2$ Molecules for Coinage Metals (Absorptions above 400 cm^{-1} Are Listed)

	obsd frequencies			
	Ar	Ne	calcd frequencies[a]	assignment
NF_3	1028.1	1029.3	1034.1 (48)	sym. N−F str.
	898.1	901.3	874.4 (258 × 2)	asym. N−F str.
	648.9	645.1	645.3 (3)	sym. NF_3 deform.
	494.9	492.4	484.9 (2 × 2)	asym. NF_3 deform.
F_2NCuF	1090.5	1094.3	1117.4 (369)	sym. F−N−F str.
	985.0	988.2	971.9 (187)	asym. F−N−F str.
	678.4	[b]	664.1 (83)	$^{63}Cu-F$ str.[c]
	597.5	[b]	588.9 (11)	NF_2 bend.
F_2NAgF	1099.2	1102.4	1083.1 (421)	sym. F−N−F str.
	1006.3	1010.8	979.2 (207)	asym. F−N−F str.
	[b]	[b]	591.2 (1)	NF_2 bend.
	529.6	[b]	531.0 (72)	Ag−F str.
F_2NAuF	1089.7	1095.3	1077.4 (416)	sym. F−N−F str.
	1013.4	[b]	982.9 (185)	asym. F−N−F str.
	[b]	[b]	605.1 (8)	NF_2 bend.
	[b]	[b]	572.7 (73)	Au−F str.
$FNCuF_2$	1139.6	[b]	1189.0 (267)	N−F str.
	736.2	[b]	707.7 (136)	asym. $F-^{63}Cu-F$ str.[d]
	[b]	[b]	564.2 (10)	sym. $F-^{63}Cu-F$ str.
$FNAgF_2$ [e]			1157.5 (340)	N−F str.
			610.3 (111)	asym. F−Ag−F str.
			509.0 (8)	sym. F−Ag−F str.
$FNAuF_2$ [e]			1096.8 (337)	N−F str.
			605.4 (122)	asym. F−Au−F str.
			559.2 (18)	sym. F−Au−F str.
			541.5 (14)	Au−NF str.

[a]Frequencies in cm^{-1} and intensities (in parentheses) in km/mol. [b]Not observed. [c] $^{65}Cu-F$ str. observed at 675.5 cm^{-1} and calculated at 661.1 cm^{-1}. [d]Asym. $F-^{65}Cu-F$ str. observed at 732.1 cm^{-1} and calculated at 703.6 cm^{-1}. [e]Not formed.

Two weak absorptions at 1089.7 and 1013.4 cm^{-1} were observed in the reactions of Au and NF_3 in solid argon (Figure 3). They are most probably due to the symmetric and antisymmetric F−N−F stretching modes of the F_2NAuF molecule, respectively, based on the band positions as well as the small matrix shifts from neon to argon.

The assignments of the F_2NMF (M = Cu, Ag, Au) molecules are supported by density functional calculations at the B3LYP level of theory. For the F_2NCuF product, the $^2B_1$ state with planar C_{2v} symmetry is found to be the ground state (Figure 5). Four infrared absorptions at 1117.4, 971.9, 664.1, and 588.9 cm^{-1} are predicted above 400 cm^{-1} from frequency calculations. The first two bands are due to symmetric and antisymmetric F−N−F stretching modes of the NF_2 fragment with the former being twice as strong as the latter one. The positions of these two bands are slightly higher and lower than the observed frequencies, which is similar to our results for NF_3 (Table 1) and in the range of agreement found for other simple molecules.[32] The Cu−F stretching mode is predicted at 664.1 cm^{-1} with a copper isotopic splitting of 3.0 cm^{-1}, almost the same as the experimental value. For the NF_2 bending mode, the

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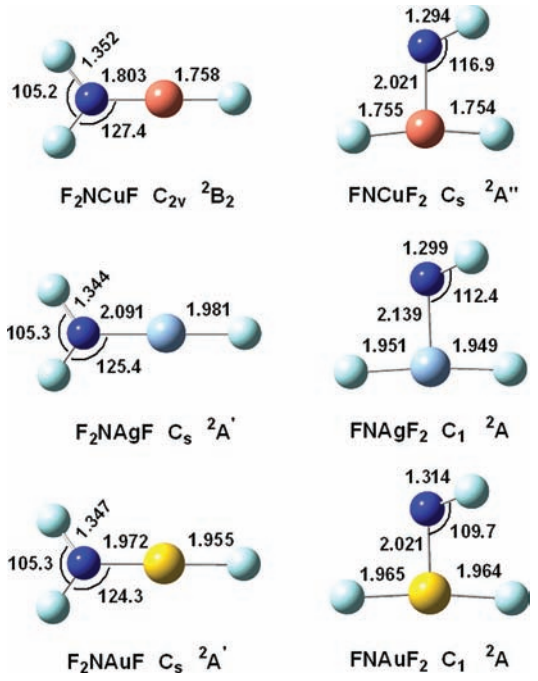

Figure 5. Structures of the F_2NMF and $FNMF_2$ (M = coinage metals) molecules calculated at the DFT/B3LYP level of theory (bond lengths are in Ångstrom units, and bond angles are in degrees).

calculated 588.9 cm^{-1} band is also close to the experimental frequency at 597.5 cm^{-1}.

The F_2NAgF molecule also possesses a doublet ground state with slightly distorted C_{2v} symmetry, as evidence by the sum of two Ag−N−F and one F−N−F angle (356.1°) (Figure 5). Similar with the copper product, our calculations reveal that the F_2NAgF molecule has four absorptions at 1083.1, 979.2, 591.2, and 531.0 cm^{-1} above 400 cm^{-1}. However, the 591.2 cm^{-1} band due to the NF_2 bending mode is too weak (Table 1), which results in its absence in the experiment. The calculated 1083.1 and 979.2 cm^{-1} absorptions are slightly lower than the experimentally observed symmetric and antisymmetric F−N−F stretching modes. Calculations on the silver isotopes reveal that the Ag−F stretching mode for the $F_2N^{107}AgF$ and $F_2N^{109}AgF$ molecules are only separated by 0.8 cm^{-1}, which is too small to be resolved experimentally. As a result, only a single band is observed for this mode. The F_2NAuF molecule is calculated to have very strong absorptions at 1077.4 and 982.9 cm^{-1} with relative intensities of approximately 2:1, which fit the experimental frequencies at 1089.7 and 1013.4 cm^{-1}. While the weaker absorptions of NF_2 bending and Au−F stretching modes are predicted at 605.1 and 572.7 cm^{-1}, they were not observed due to the low yield of the F_2NAuF molecule.

As shown in Figure 5, the M−F bond lengths (M = coinage metals) increase from copper to silver but slightly decrease for gold, which is also the trend observed for the coinage metal fluoride molecules.[30] The shorter bond lengths for the gold-containing molecules result from the relativistic effects of gold.[33] A similar trend is observed for the calculated M−N distances. The Ag−N bond length is calculated to be 2.091, 0.119, and 0.288 Å longer than those of gold and copper. To compare further the M−N bond strengths of different coinage metals, the dissociation energies of the F_2N−MF bonds are calculated at the B3LYP level of theory. It is found that the Cu−N (27.5 kcal/mol) and Au−N (26.5 kcal/mol) bonds are stronger than that of silver (12.2 kcal/mol), which is also in line with changes in the M−N bond lengths. Recent gas phase studies on the dimethylaminonitrene complexes of coinage metals revealed that the M−N bond strengths for copper and gold are similar but about 5 kcal/mol higher than that of silver.[34] This is consistent with the fact that silver has the longest bond length followed by gold and copper. It appears that this kind of change in bond lengths and strengths is common for coinage metals, which is also the case for the M−C bonds in the CH_3MH and CH_3MF molecules produced from the reactions of coinage metals with CH_4 and CH_3F.[35,36]

The molecular orbitals of the F_2NMF molecules reveal that the unpaired electron is delocalized over the whole molecule, which contains some M−N π^* character in addition to the doubly occupied π orbital. Hence, beyond the M−N σ bond, the M−N bond also exhibits weak π interactions due to its singly occupied nature. Actually, the Cu−N distance (1.803 Å) is slightly lower than the sum of copper and nitrogen single bond radii,[37] suggesting that the Cu−N bond in the F_2NCuF molecule is slightly more than a single bond. Recent theoretical and experimental studies on the copper nitrene species also gave similar Cu−N bond distances, which are expected to have some Cu−N double bond character.[6,9] For the F_2NAuF molecule, the calculated Au−N bond length of 1.972 Å is about 0.04 Å shorter than the value in the amido gold complex.[10] The recently identified CH_2AuF molecule was proposed to have a Au═C double bond with some π character.[35] Spin density calculations for all three molecules predict that most of the electron spin density is on nitrogen atom (more than 65%), which contributes to the weak π interactions.

$FNCuF_2$. Three absorptions at 1139.6, 736.2, and 732.1 cm^{-1} were produced upon $\lambda > 290$ nm irradiation, during which the F_2NCuF absorptions disappeared. Hence, these new bands could arise from a structural isomer of the F_2NCuF molecule. The 736.2 and 732.1 cm^{-1} absorptions are about 7 cm^{-1} red-shifted from the isolated CuF_2 band, and the 4.1 cm^{-1} split is almost the same as that of CuF_2 (4.2 cm^{-1}) observed in the same experiment. As a result, these two bands are assigned to the antisymmetric F−^{63}Cu−F and F−^{65}Cu−F stretching modes of the new molecule. The 1139.6 cm^{-1} band should be an N−F stretching vibrational mode on the basis of the band position. Hence, a $FNCuF_2$ complex with NF and CuF_2 subgroups is proposed as the most probable origin of the new absorptions. Earlier matrix infrared spectra of the CuF_2 molecule produced from evaporation of bulk material revealed two weak matrix site bands of CuF_2 at 736.5 and 732.6 cm^{-1},[38] which were not observed in our recent experiments on the reactions of laser-ablated copper atoms and F_2.[30] It is obvious that the appearance of the 1139.6 cm^{-1} absorption together with the 736.2 and 732.1 cm^{-1} bands provides adequate evidence for the assignment of the $FNCuF_2$ complex in our current experiments.

Calculations at B3LYP level of theory reveal that the $FNCuF_2$ molecule has a planar geometry and doublet ground state (Figure 5). The N−F stretching mode is predicted at 1189.0 cm^{-1}, which is also the strongest band of the product. For the CuF_2 moiety, the antisymmetric and symmetric F−Cu−F modes are calculated at 707.7 and 564.2 cm^{-1} with the relative intensities of 13:1 (Table 1). Experimentally, the product absorptions are observed at 1139.6 and 736.2 cm^{-1}, while the symmetric F−Cu−F mode is too weak to be observed here. In addition, the splitting for the antisymmetric F−Cu−F

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stretching mode due to copper isotopes is calculated to be 4.1 cm^{-1}, the same as the experimental value. The Cu−N distance is predicted to be 2.021 Å, about 0.2 Å longer than that in the F_2NCuF molecule as well as the bond length proposed for single Cu−N bond.[37] The calculated dissociation energy of the FN−CuF_2 bond is 11.9 kcal/mol [relative to CuF_2 and ($^3\Sigma$) NF], less than half of the value for the Cu−N bond in the F_2NCuF molecule, suggesting that CuF_2 and NF are weakly bound in the $FNCuF_2$ molecule. This is also consistent with the longer computed Cu−N bond length in the $FNCuF_2$ molecule. Although a nitrene complex might be expected in this case due to the availability of two electrons on nitrogen, the formation of a Cu═N double bond would require a copper(IV) center, which is an uncommon oxidation state for copper.[39] We find no evidence for CuF_4 in ongoing fluorine work in this laboratory,[30] despite the fact that the neutral CuF_4 molecule was predicted to be stable.[40] In summary, the $FNCuF_2$ molecule contains a long computed Cu−N bond length with a Cu(II)-like metal center.

In addition to the observed $FNCuF_2$ molecule, calculations using the B3LYP functional are also performed on the unobserved silver and gold analogs. As shown in Figure 5, the optimized structures of the $FNAgF_2$ and $FNAuF_2$ molecules are quite similar. Both of them have doublet ground states with the N−F moiety slightly out of the F_2AgN and F_2AuN plane. The Ag−N and Au−N bond distances are only slightly longer (about 0.05 Å) than those in the F_2NAgF and F_2NAuF molecules with the Ag−N and Au−N bond energies calculated to be 10.1 and 19.0 kcal/mol, suggesting that the metal nitrogen bonds are also weakened upon the second fluorine transfer but not as much as that for copper. Frequency calculations reveal that both of them have strong N−F stretching absorptions around 1100 cm^{-1} followed by strong metal−fluorine stretches around 600 cm^{-1} (Table 1).

Reactions in the Matrix. As shown in Figures 1−3, the F_2NMF (M = coinage metal) molecules are produced spontaneously via the reactions of coinage metals with NF_3 upon sample annealing. This is in contrast to the copper reaction with ammonia, which required irradiation for insertion into the N−H bond.[13] No $M(NF_3)$ complexes were observed in the experiments. Our geometry optimizations on the different structures of molecular complexes give rather long N−M or F−M distances. Hence, the $M(NF_3)$ complexes are not stable minima along the reaction coordinates of coinage metals and NF_3. The spontaneous productions of the F_2NMF molecules indicate that negligible activation energies are required for one fluorine transfer from NF_3 to the coinage metals. Reactions (1) for coinage metals are predicted to be exothermic with copper being the highest followed by gold and silver (Table 2). Note that all of the coinage metals in the

Table 2. Computed (B3LYP) Energies (Relative to Ground State Coinage Metal Atoms and NF_3, kcal/mol) of the F_2NMF and $FNMF_2$ Molecules as Well as the Transition States

	F_2NMF	TS	$FNMF_2$
Cu	−68.3	−50.3	−63.8
Ag	−35.4	−4.5	−15.4
Au	−37.1	−3.9	−22.5

F_2NMF molecules are in the II oxidation state. Although this is common for species with copper and divalent silver fluorides and oxides are also available,[30,41] molecules with a mononuclear gold(II) centers are not as common as the gold(I) and (III) species due to the tendency of disproportionation for Au(II) to the other two oxidation states.[42] Our recent studies revealed that divalent gold species can be prepared via insertion into the single bond of some simple molecules.[35,36,43,44]

$$M + NF_3 \rightarrow F_2NMF \quad (1)$$

Different from the NF_3 reactions reported here, thermally evaporated copper atoms reacted with ammonia in solid argon to give the $Cu(NH_3)$ complex first, which isomerized to $HCuNH_2$ upon UV irradiation via N−H bond insertion.[13] The $Cu(NH_3)$ complex was characterized to have a direct Cu−N interaction from theoretical calculations.[45] However, no similar $Cu(NF_3)$ complex was observed in the reactions of Cu and NF_3, which is also supported by the spontaneous formation of the F_2NCuF molecule on annealing. The weak N−F bond makes the insertion reaction easier than that for N−H bond,[17] which probably accounts for the spontaneous formation of the F_2NCuF molecule. Because fluorine is the most electronegative atom, the lone pair electronic density of NF_3 is reduced, and the dipole moment direction is also reversed as compared with those of NH_3,[46] both of which make it less favorable to form the $Cu(NF_3)$ complex with a Cu−N interaction. This is also consistent with our results on the geometry optimizations of the $Cu(NF_3)$ system. Note that NF_3 is a very weak base and can only form a weakly bonded complex with BF_3 (B−N dissociation energy, 1.8 kcal/mol), and BF_3 is known as a strong Lewis acid. In contrast, the binding energy of the F_3B−NH_3 adduct is more than 20 kcal/mol.[47]

In the reactions of copper and NF_3, the $FNCuF_2$ isomer is identified on the basis of the N−F and F−Cu−F stretching modes. However, no trace can be found for the formation of similar products in the silver and gold reactions under the same conditions, suggesting that it is not favorable to form the analogous molecules with heavier coinage metals. Calculations on the isomerization pathways between F_2NMF and $FNMF_2$ isomers reveal that the formation of the $FNCuF_2$ molecule is prohibited by an energy barrier of 18.0 kcal/mol, while the activation energies for silver and gold are calculated to be 30.9 and 33.2 kcal/mol (Table 2). Because the barrier heights for producing $FNAgF_2$ and $FNAuF_2$ molecules are about twice as high as that for copper, formations of these heavier analogs are not favored because of kinetic reasons. Although the UV photon energies used are higher than the energy barriers for all of the metals, the successful formation of the isomerization products also requires access to the corresponding excited electronic states of $FNAgF_2$ and $FNAuF_2$, which probably do not happen with the radiation employed. These excited states are not calculated theoretically here. In addition, our calculations also indicate that formation of the $FNCuF_2$ molecule is more favorable thermodynamically. The $FNCuF_2$ molecule is predicted to be only 4.5 kcal/mol less stable than the F_2NCuF isomer, while the values for silver and gold are 20.0 and 14.6 kcal/mol, respectively. After $FNCuF_2$ was produced by $\lambda > 290$ nm irradiation, annealing to 30 K sharpened these absorptions, but annealing to 35 K slightly decreased these bands (Figure S1 in the Supporting Information). Annealing to such "high" temperature as 35 K in solid argon allows diffusion and aggregation of isolated species, and these aggregates have broader absorptions than the previously isolated species, which is common in matrix infrared spectroscopy.[22]

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The F_2NMF molecules were all photosensitive: F_2NCuF was completely destroyed by $\lambda > 290$ nm irradiation, and the $FNCuF_2$ isomer as well as NF and NF_2 species were produced. In the Ag and Au experiments, $\lambda > 290$ nm irradiation initiated the formation of NF and NF_2, and $\lambda > 220$ nm irradiation slightly continued the growth of NF, while both F_2NAgF and F_2NAuF absorptions decreased. Figure S1 (Supporting Information) shows expanded scale spectra in the important 1160−1060 and 760−720 cm^{-1} regions containing all of the experimental changes from the Cu and NF_3 reactions (^{63}Cu and ^{65}Cu isotopes observed for CuF_2 and $FNCuF_2$ are indicated). Because NF and NF_2 were not observed in the blank experiment without metal atoms, decomposition of the F_2NMF molecules to NF and NF_2 species should be considered. Also, we could not rule out nor detect any reformation of coinage metals and NF_3 because metal atoms do not have absorptions in the midinfrared region, while the NF_3 precursor bands are huge and their band shapes change upon sample annealing and irradiation. Although reactions of metal atoms with NF and NF_2 are possible, the weaker intensities of these species as compared with NF_3 makes it unlikely for them to form enough molecules to be detected by matrix infrared spectroscopy.

The recently reported $N{\equiv}MF_3$ (M = group VI and uranium) molecules were characterized to have triple metal−nitrogen bonds,[18,19] while the pnictinidene $N{\div}MF_3$ molecules with two radical π bonds were produced for group IV and thorium atoms.[20] All of these species are found to be most stable among the products from stepwise fluorine transfer reactions. However, reactions of coinage metals and NF_3 give the F_2NMF molecules as the most stable products. The two fluorine transfer molecules are higher in energy, which is apparently the result of the weak $FN{-}MF_2$ bonds since both the N−F and the coinage metal−F bond strengths are comparable.[48,49] For uranium and group VI metals, the M−N bond orders increase with the stepwise transfer of fluorine from nitrogen to metal center, which is expected to be energetically favorable.[18,19] The VI oxidation state also makes it possible for the formation of triply bonded species. The pnictinidene $N{\div}MF_3$ molecules satisfies the IV oxidation state of group IV and thorium atoms, and formation of the strong M−F bonds provides the driving force for the fluorine transfer from nitrogen to metal.[20]

The spectra from the reactions of coinage metals with NF_3 also show some other features in addition to the product bands mentioned above. New absorptions on the lower sides of the CuF_2 and AuF_2 bands and higher side of the AgF_2 band were produced in different experiments. The 738.4 and 734.0 cm^{-1} absorptions observed in the copper experiment show a similar splitting with CuF_2 due to copper isotopes, suggesting that a new complex of CuF_2 is formed here (Figure S1 in the Supporting Information). The most probable assignment for the new species is the $(NF_3)CuF_2$ complex since the amount of NF_3 is much more than other molecules in the same matrix sample. Similar tentative assignments can be made to the doublet band (625.4 and 623.9 cm^{-1}) produced in the silver experiments and the single band observed at 630.7 cm^{-1} for gold. Our B3LYP calculations predict that all of the $(NF_3)MF_2$ complexes (M = coinage metal) with some metal nitrogen interactions are stable. In the N−F stretching region, some weak metal-dependent absorptions were observed as well, which probably track the lower fluoride stretching modes and arise from the N−F stretching vibrations of the $(NF_3)MF_2$ complexes.

CONCLUSIONS

The reactions of coinage metals (Cu, Ag, Au) with NF_3 have been studied in argon and neon matrixes. Reaction products are characterized by infrared spectroscopy and density functional calculations. Ground state coinage metal atoms react with NF_3 spontaneously to give the amido F_2NMF molecules via insertion into the weak N−F bond during sample annealing. All three products are predicted to have doublet ground states with C_{2v} or near C_{2v} geometries. Both the bond lengths and the energies suggest strong M−N interactions, which are believed to be slightly more than single bonds. The Ag−N bond is found to be longer and weaker than that of the other two coinage metals. No trace can be found for the formation of the $M(NF_3)$ complexes, which are also predicted to be unstable along the reaction coordinates of coinage metals and NF_3. UV−visible irradiation induces formation of the less stable $FNCuF_2$ isomer with a weaker Cu−N bond, while the silver and gold analogs are not observed, the formation of which are both kinetically and thermodynamically less favorable than that of $FNCuF_2$. Our calculations suggest that the M−N bonds of the $FNMF_2$ isomers are weaker and longer than those of the F_2NMF molecules.

ASSOCIATED CONTENT

Supporting Information

Figure S1 of expanded scale infrared spectra from an experiment using Cu and NF_3 and from a blank experiment with argon/NF_3 and no metal atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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