tributed to this particular transition.

3. Attempted Correlations of the UV–Visible, Raman, ^{13}C NMR, and X-ray Diffraction Data. Table I presents some spectroscopic results for free and complexed isocyanide ligands. It is known that in going from CNMe to CN-*t*-Bu, there is a decrease in s character of the σ-bonding orbital for the free ligand.[46] The order of ^{13}C NMR shifts observed for the terminal carbon (carbene) in the CNR ligands with changes in R is xylenyl ≫ Me > *t*-Bu. The decrease in ν(CN) with increasing size of the R group, Me < benzyl < *t*-Bu and xylenyl, indicates a decrease in N–C bond strength. On the basis of ^{13}C NMR[46] and vibrational data,[25] the xylenyl isocyanide ligand has a large amount of sp^2 character at its terminal carbon atom. Stephany et al.[46] have suggested that bending of the CNC angle could take place due to the bulkiness of the alkyl R groups.[47] Consequently, there is a rehybridization of the N atom from sp to sp^2, thereby explaining the decrease in ν(CN). The UV–visible data given in Table I suggest that for complexed ligands, the σ-donor capacities should decrease in the order xylenyl ≫ benzyl ~ *t*-Bu > Me, in disagreement with the ^{13}C NMR results for the free ligands. Therefore, the σ-donor properties are modified during substitution as evidenced by the change in ν(CN) between the free and complexed ligand (there is an increase in s character in N–C bond). When *n* is changed, ν(CN) remains essentially unchanged, indicating that the CN bond distances and CNC angles remain the same from complex to complex. Since the value of ν(CN) in the complexes increases as xylenyl < *t*-Bu < benzyl < Me, it is believed that this same order represents the order of decreasing σ-capacity of the linear isocyanide ligands (in agreement with the UV–visible results). Thus, the relative σ-donor and π-acceptor properties of the complexed isocyanides estimated by electronic spectroscopy seem to correlate reasonably well with the Raman results.

The actual Re–Re distances are as follows: $Re_2(CO)_{10}$, 3.041 (1) Å;[22] $Re_2(CO)_9$(CN-*t*-Bu), 3.048 (1) Å;[19] $Re_2(CO)_8(CN(2,6\text{-}Me_2C_6H_3))_2$, 3.048 (1) Å;[20] $Re_2(CO)_7(CN(CH_2C_6H_5))_3$, 3.049 (1) Å;[20] Re2$(CO)_6(CN(2,6\text{-}Me_2C_6H_3))_4$, 3.079 (1) Å.[20] The weakening of the M–M bond in $M_2(CO)_{10}$ and $MM'(CO)_{10}$ complexes (M and M′ = Mn, Tc, Re) has been discussed by Brown et al.[48] Woodruff[49] derived an empirical equation relating the M–M force constant (F/mdyn Å^{-1}) and the M–M separation (r/Å) for the 5d element:

$$r(5d) = 2.01 + 1.31\exp(-F/2.36) \qquad (1)$$

Woodruff calculated the Re–Re separation (3.01 Å), and it appears to be 0.03 Å shorter than the one evaluated by crystallography. Using the previously published Raman data,[25] we obtained similar results for our complexes. The problems that are encountered here are the facts that this relationship is not accurate enough to take into account small perturbations and the M–M stretching modes are extensively mixed for these complexes.

Since we know that electronic spectroscopy looks at electronic transitions only, the problem with the vibrational spectroscopy of $Re_2(CO)_{10-n}(CNR)_n$ complexes seems to be resolved. Our experimental results have shown clear monotonic progressions of the $d\sigma^* \leftarrow d\sigma$ position versus *n* (see Figures 2–4). The accuracy of the experimental method is reasonable at room temperature and particularly good at 77 K. To date, no empirical relationship between the metal–metal separations and metal-to-metal electronic transitions exists. Unfortunately, it is clear that due to the lack of crystallographic data, very little can be done in this respect. Nevertheless, there is an apparent correlation between the metal–metal bond length and the $d\sigma^* \leftarrow d\sigma$ band positions for the xylenyl complexes (three data points), and a monotonic bond lengthening is expected with increase of *n*.

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Registry No. $Re_2(CO)_{10}$, 14285-68-8; $Re_2(CO)_9$(CNMe), 95672-45-0; $Re_2(CO)_9$(CN-*t*-Bu), 95463-95-9; $Re_2(CO)_9$(CNBz), 95590-07-1; $Re_2(CO)_9$(CNXy), 95590-13-9; $Re_2(CO)_8(CNMe)_2$ (1,1′-isomer), 95590-17-3; $Re_2(CO)_8(CNMe)_2$ (1,2-isomer), 95590-16-2; $Re_2(CO)_8$(CN-*t*-Bu)$_2$ (1,1′-isomer), 95672-44-9; $Re_2(CO)_8$(CN-*t*-Bu)$_2$ (1,2-isomer), 95590-05-9; $Re_2(CO)_8(CNBz)_2$, 95590-08-2; $Re_2(CO)_8(CNXy)_2$, 95406-94-3; $Re_2(CO)_7(CNMe)_3$, 95406-95-4; $Re_2(CO)_7$(CN-*t*-Bu)$_3$, 95590-06-0; $Re_2(CO)_7(CNBz)_3$, 95590-09-3; $Re_2(CO)_7(CNXy)_3$, 95590-14-0; $Re_2(CO)_6(CNXy)_4$, 95406-96-5.

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Infrared Spectra of Hydrazine and Products of Its Reactions with HF, F_2, and O_3 in Solid Argon

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Hydrazine, N_2H_4, and its reactions with HF, F_2, and O_3 have been studied in an argon matrix. Vibrational assignments have been made for hydrazine, including clarification of the ν_6, ν_{10}, and $2\nu_7$ bands. Complexation of N_2H_4 with HF produced a strong band at 2928 cm^{-1} (ν_s(HF)) and sharp bands at 940 and 922 cm^{-1} (ν_l(HF)), as well as several perturbed N_2H_4 submolecule absorptions; the frequencies of these bands suggest a chelated structure similar to that for the NH_2OH–HF complex. Hydrazine and fluorine reacted during deposition to give the NH_2NHF–HF complex (ν_s = 3113 cm^{-1}, ν_l = 726, 680 cm^{-1}). Reaction of hydrazine and ozone produced hydroxyhydrazine, NH_2NHOH, and minor products during deposition; photolysis increased the yield of hydroxyhydrazine. Evidence for an intramolecular hydrogen bond was found for NH_2NHOH. This matrix study presents the first spectroscopic evidence for both NH_2NHF and NH_2NHOH.

Introduction

One of the advantages of the matrix isolation technique over other spectroscopic methods is that it can be used to study reactive molecules and intermediates that would otherwise be difficult to observe. An example of such a molecule is hydrazine, which is sufficiently reactive to have been used as a rocket fuel.[1] Past experiments involving hydrazine in the gas phase,[2–5] in a N_2 matrix,[6] and as a salt[7] have shown some disagreement in vibra-

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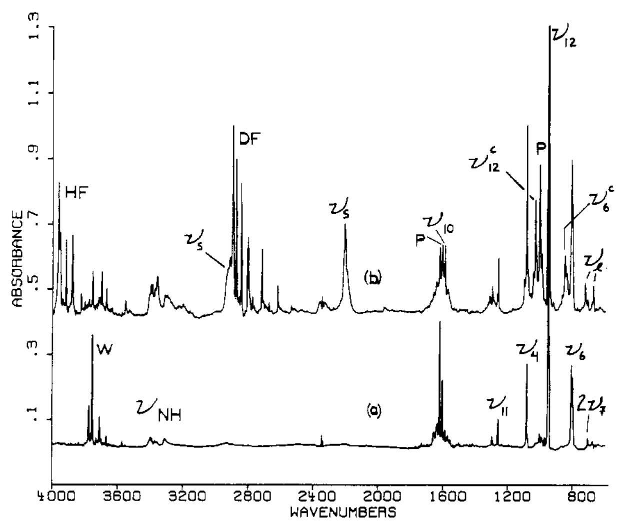

Figure 1. (a) Infrared spectrum of Ar/N_2H_4 (approximately 1000:1) sample deposited at 12 K. W = H_2O absorptions. (b) Infrared spectrum of Ar/N_2H_4 (approximately 500:1) and Ar/HF/DF (100:1) codeposited at 12 K. P = N_2H_4 polymer absorptions.

tional assignments. Also, intermediates have been observed and characterized for the $N_2H_4 + F_2$ and $N_2H_4 + O_3$ reactions, yielding new clues about mechanisms of hydrazine reactions.

Hydrazine is also interesting in terms of ongoing studies on the hydrogen-bonded complexes of HF and substituted amines in this laboratory. Past studies have investigated NH_3,[8] NH_2OH,[9] NH_2F,[10] NH_2CN,[11] and NH_2CH_3.[12] From such spectroscopic studies estimates can be made of the relative electron-donating or electron-withdrawing strengths of these substituents and their effect on the amine basicity.

Experimental Section

The vacuum apparatus and cryogenic techniques have been described previously.[13,14] Spectra of N_2H_4 and HF, F_2, and O_3 were recorded on a Perkin-Elmer 983 dispersive infrared spectrometer from 4000 to 180 cm^{-1}, with a frequency accuracy of ±0.5 cm^{-1}. A Nicolet 7199 FT-IR spectrometer was used to record spectra of N_2H_4 and DF from 4000 to 400 cm^{-1}, with a resolution of 1.0 cm^{-1} and a frequency accuracy of ±0.3 cm^{-1}. Spectra of N_2H_4 in solid argon were recorded on both instruments. Anhydrous hydrazine (Aldrich) was transfered under dry nitrogen through a Teflon stopcock into a Pyrex finger containing NaOH pellets; N_2H_4 vapor was introduced into the matrix by evaporation from the liquid at −78 °C through the Teflon stopcock and deposition tube. Hydrogen fluoride gas (Matheson) was outgassed at 77 K and diluted with argon to concentrations ranging from 100:1 to 400:1 (Ar:HF). Deuterium fluoride was synthesized by mixing equimolar amounts of F_2 (Matheson) and D_2 (Air Products) sufficient to make 1 mmol of gas in a passivated stainless-steel can. The DF was then diluted in argon in the same manner as HF. F_2 (Matheson) was diluted with argon as above. Ozone was generated by Tesla coil discharge of oxygen (normal isotopic or ^{18}O-enriched gas) in a Pyrex tube immersed in liquid N_2: residual O_2 was removed at 77 K, and O_3 was diluted with Ar as above.[15]

Table I. Infrared Absorptions (cm^{-1}) and Assignments for Hydrazine

absorptions: solid argon	absorptions: gas[a]	intens[b]	assignt[a]
3397	3325	w	$\nu_1(A)$
3390		vw	ν_1 (polymer)
3371	3350	vw	$\nu_8(B)$
3358		vw	ν_8 (polymer)
3310	3280	w	$\nu_9(B)$
1608	1628		ν_{10} (polymer)
1591	1587		$\nu_{10}(B)$
1300	1493	vw	ν_3(tent)
1267		vw	ν_{11} (site)
1261	1275	w	$\nu_{11}(B)$
1086	1098	m	$\nu_4(A)$
1007		w	polymer
991		vw	polymer
953	933, 966	vs	$\nu_{12}(B)$
812	780	m	$\nu_6(A)$
804		m	ν_6 (site)
708		vw	$2\nu_7$
388	374	m	ν_7
372		w	ν_7 (site)

[a] Gas-phase frequencies and assignments are based on ref 2. [b] vw = very weak, w = weak, m = medium, s = strong.

Table II. Absorptions (cm^{-1}) and Assignments for Hydrazine–HF Complex Products

assignt	freq: N_2H_4	freq: N_2H_4–HF	freq: N_2H_4–DF
ν_s		2928	2210
$\nu_l(A)$		922	673
$\nu_l(B)$		940	723
ν_{sa}		1966	
$\nu_4(A)$	1086	1094	(1094)
$\nu_6(A)$	812	838	850
$\nu_{12}(B)$	954	1043	1032

Spectra were recorded after a deposition of the N_2H_4 and Ar/X (X = HF, F_2, O_3) samples for 4–6 h at 3–5 mmol/h onto a 12 K CsI window suspended in a 10^{-7} Torr vacuum. In the F_2 and O_3 experiments, the matrix was then subjected to photolysis by using as BH-6 high pressure mercury arc lamp (1000 W, Illumination Industries Inc.) for periods up to 1.0 h. As a final step, in all experiments (except for ozone) samples were annealed by heat cycling from 12–24–12 K in order to allow diffusion and further association of trapped species, and additional spectra were taken to characterize the diffusion products.

Results

N_2H_4. Preliminary experiments were performed with deposition of only hydrazine in the argon matrix. Various sample concentrations and deposition rates were used to characterize monomeric and polymeric bands. Figure 1a shows a typical spectrum, with an $Ar:N_2H_4$ concentration of approximately 1000:1 and an argon deposition rate of 3–5 mmol/h.

Prominent absorptions include a pair of sharp bands at 1608 and 1591 cm^{-1} (labeled P for N_2H_4 polymer and ν_{10} for the N_2H_4 fundamental), a sharp weak band at 1261 cm^{-1} (ν_{11}), a sharp band at 1086 cm^{-1} (ν_4), a weak band at 1007 cm^{-1} (P), a strong band at 953 cm^{-1} (ν_{12}), a doublet at 812 and 804 cm^{-1} (ν_6), a weak band at 708 cm^{-1} ($2\nu_7$), and a strong band at 388 cm^{-1} with a resolved companion at 372 cm^{-1} (ν_7). These and other absorptions are listed in Table I.

N_2H_4 + HF. Codeposition of N_2H_4 and HF produced absorptions characteristic of both the base and acid, as well as bands that did not appear on deposition of either the acid or base alone. The representative spectrum shown in Figure 1b employed an Ar:HF ratio of 200:1. Characteristic HF system absorptions observed include $(HF)_2$, $(HF)_3$, H_2O, H_2O–HF, and N_2–HF.[16]

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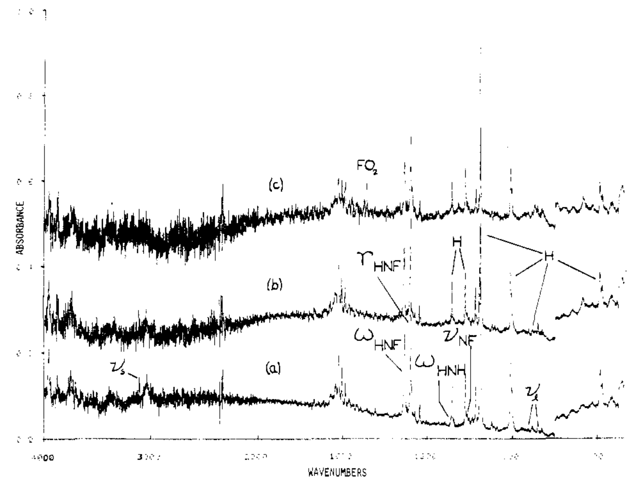

Figure 2. Infrared spectra of $Ar/N_2H_4/F_2$ sample at 12 K: (a) spectrum of Ar/N_2H_4 (approximately 500:1) and Ar/F_2 (100:1) codeposited at 12 K; (b) spectrum after 1.0-h Hg arc photolysis; (c) spectrum after warming to 24 K and cooling to 12 K. H = N_2H_4 absorptions, with ordinate in absorbance units.

Table III. Absorptions (cm^{-1}) and Assignments for Hydrazine-Fluorine Reaction Products

freq	assignt	freq	assignt
3113	ν_s	1282	NHF rock
726, 680	ν_l	1091	HNH wag
1311	NHF wag	1013	NF stretch

Bands that appeared on deposition of only hydrazine are labeled ν_i if they represent fundamental absorptions or P if they are due to $(N_2H_4)_n$.

Bands that appeared only on codeposition of the two species include a broad, intense band at 2928 cm^{-1} (labeled ν_s) ($A = 0.4$; full width at half-maximum (fwhm) = 30 cm^{-1}), two sharp absorptions at 940 and 922 cm^{-1} (ν_l(B) and ν_l(A), respectively), and a weak, broad band at 1966 cm^{-1} (ν_{sa}). The 2928-, 940-, and 922-cm^{-1} bands behaved similarly on annealing, decreasing significantly, while the 1966-cm^{-1} band increased; also, the 1966-cm^{-1} band became more intense relative to the other three as the concentration of HF in the Ar/HF mixture was increased. Other new absorptions noted include bands at 1094, 1043, and 838 cm^{-1} ($\nu_4{}^c$, $\nu_{12}{}^c$, and $\nu_6{}^c$). These bands are summarized in Table II.

Substitution of DF for HF produced several new absorptions, as shown in Figure 1b. Due to HF impurity, the bands described above were seen again. New bands due to DF polymer and DF complexes with water and nitrogen impurities are labeled accordingly. Also observed were a broad band at 2210 cm^{-1} (ν_s), weak, sharp bands at 723 and 673 cm^{-1} (ν_l(B) and ν_l(A)), and strong, sharp bands at 1032 and 850 cm^{-1} ($\nu_{12}{}^c$ and $\nu_6{}^c$). These bands can also be found in Table II.

$N_2H_4 + F_2$. Codeposition of hydrazine and fluorine resulted in the appearance of hydrazine bands mentioned above, weak NH_3 bands from hydrazine decomposition, impurities common to F_2 experiments, and new bands not seen on deposition of either reagent alone. These new bands include a weak, sharp peak at 3113 cm^{-1} (ν_s), a weak, broad band at 3044 cm^{-1}, a strong band at 1311 cm^{-1} (ω_{HNF}), a strong, sharp band at 1282 cm^{-1} (γ_{HNF}), a weak band at 1091 cm^{-1} (ω_{HNH}), a weak, broad peak at 1013 cm^{-1} (ν_{NF}), and weak bands at 726 and 680 cm^{-1} (ν_l). Photolysis produced no new bands. Annealing to 28 K produced only a doublet of sharp bands near 1490 cm^{-1}, attributable to FO_2, and decreased the new bands noted above approximately 25%. A typical spectrum, with an Ar:F_2 ratio of 100:1 and an approximate Ar:N_2H_4 ratio of 500:1, is shown in Figure 2. These results are shown in Table III.

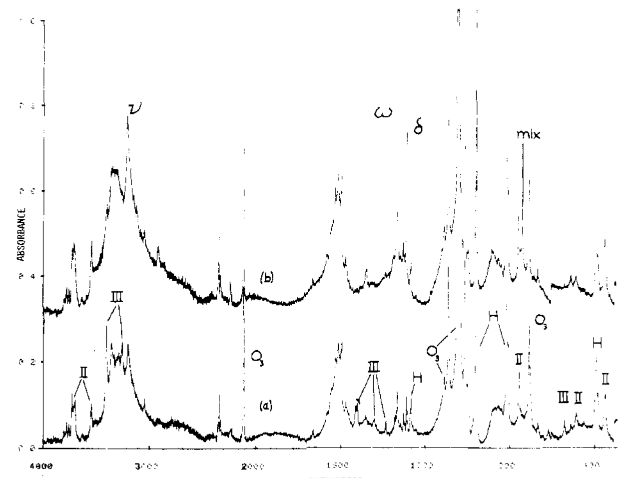

Figure 3. Infrared spectra of $Ar/N_2H_4/O_3$ sample at 12 K: (a) spectrum of Ar/N_2H_4 (approximately 500:1) and Ar/O_3 (200:1) codeposited at 12 K; (b) spectrum after 1.0 h Hg arc photolysis. H = N_2H_4 absorptions; O_3 = ozone absorptions; ν_{OH}, $\omega_{NH(OH)}$, δ_{NNH}, and "mix" belong to Class I photolysis species; ordinate is in absorbance units.

Table IV. Absorptions (cm^{-1}) and Assignments for Hydrazine–Ozone Reaction Products

class	$^{16}O_3$	$^{18}O_3$	assignt/notes
I[a]	3198	3191	ν_{OH}
	2910	2896	$(N_2H_4):(NH_2NHOH)$
	2232	2225	combination band[d]
	1329	1327	NH(OH) wag
	1282	1282	δ_{NNH}
	734	730	$\nu_{NO} + \delta_{NNO} + \nu_{NN}$?
II[b]	3704	3698	water complex
	3537	3525	ν_{OH}
	753	715	δ_{NO_3}[e]
	480	479	?
	342	339	torsion?
III[c]	3398	3391	water complex
	3250	3244	water complex
	1525	1525	NH motion
	1517	1517	NH motion
	1438	1406	?[f]
	1382	1352	?[f]
	535	535	?

[a] Major product, NH_2NHOH. Bands increased 5-fold on photolysis. [b] Minor product, structure unknown. Bands grew less than 20% on photolysis. [c] Minor product, structure unknown. Bands destroyed on photolysis. [d] δ_{NNH} + NH_2 wag. [e] Displayed a sextet of bands in mixed oxygen isotope experiments (753, 745, 736, 732, 723, and 715 cm^{-1}). [f] Displayed multiplets in mixed oxygen isotope experiments.

$N_2H_4 + O_3$. Codeposition of hydrazine and ozone produced bands characteristic of the two reagents, as well as bands not seen on deposition of either molecule alone. These new bands can be divided into three classes: those that grew markedly on photolysis (at least 5-fold) (hereafter referred to as class I), those that grew slightly on photolysis (class II), and those that were destroyed on photolysis (class III). A typical spectrum is shown in Figure 3.

Class I absorptions include a strong band at 3198 cm^{-1} (ν_{OH}), sharp bands at 1329 and 1282 cm^{-1} ($\omega_{NH(OH)}$ and δ_{NNH}), and a strong band at 734 cm^{-1} (mix). In $^{18}O_3$ experiments, these bands shifted to 3191, 1327, 1282, and 734 cm^{-1}, respectively.

Class II bands (labeled II) were seen at 3704, 3537, 753, 480, and 342 cm^{-1} in $^{16}O_3$ experiments and at 3698, 3525, 715, 479, and 339 cm^{-1} in $^{18}O_3$ experiments. Class III bands (labeled III) appeared at 3398, 3250, 1525, 1517, 1438, 1382, and 535 cm^{-1}, with $^{18}O_3$ counterparts at 3391, 3244, 1525, 1517, 1406, 1352, and 535 cm^{-1}. Assignments and notes for all three classes are summarized in Table IV.

Discussion

N_2H_4. The spectrum of hydrazine in an argon matrix has not been reported in the literature, although N_2H_4 in a nitrogen matrix has been described.[6] Since there is some uncertainty in the assignment of hydrazine bands,[2,6] presentation of the hydrazine/

argon spectrum will help clarify interpretation of the spectrum. Present band assignments are based on the assumption of the hydrazine hydrogens being in a gauche orientation, which yields a C_2 symmetry for the molecule. This structure has been shown to be the preferred state, as opposed to the cis (C_{2v}) or trans (C_{2h}) orientations.[17-19]

As an example of the uncertainty in band assignment, the N_2 matrix counterpart (748 cm^{-1}) of the weak band at 708 cm^{-1} in the argon matrix has been previously attributed to ν_6, the symmetric NH_2 wagging motion.[6] However, this band is much too weak to be due to the usually strong wagging mode absorption. This band does correspond better to the second harmonic of the torsional NH_2 twisting motion, which occurs at 388 cm^{-1}. The resulting overtone:fundamental ratio, 1.82, is characteristic of the anharmonic nature of the torsion vibrational potential, as is the intensity ratio of nearly 10:1 in favor of the fundamental. The ν_6 wagging motion is instead assigned to the doublet at 812 and 804 cm^{-1}, which has a more appropriate intensity for a wagging motion.

Similar uncertainty exists in the assignment of bands in the 1500–1600-cm^{-1} region. However, here the question concerns the existence of a N_2H_4 band; if one were found, it would be due to ν_{10}, the antisymmetric scissors motion of the NH_2 groups. Our efforts in this regard were hampered by the presence of water impurity, which was almost coincident with hydrazine bands. But both deviations from the normal intensity pattern of the water vibration–rotational spectrum and comparison of spectra with differing amounts of water led to the clear observation of new bands and assignment of the 1608 and 1591 cm^{-1} bands to ν_{10} of polymer and monomer, respectively.

Also, we found difficulty with the assignment of ν_3, the symmetric scissors motion. Both infrared and Raman studies have indicated that a band due to ν_3, near 1300–1350 cm^{-1}, exists.[4,5] Indeed, in solid argon there was a band at 1300 cm^{-1}, but its intensity did not track consistently with either monomer or polymer bands under changing experimental conditions. Given this situation and considering the weak nature of the band, we reserve judgement on the identity of this band.

Assignment of the remaining spectrum was relatively straightforward. Polymer bands were assigned on the basis of band growth relative to other bands with increasing deposition rate or increasing concentration. Similarly, the resolved sidebands at 804 and 374 cm^{-1} are assigned as site splittings of the ν_6 and ν_7 bands, respectively, at 812 and 388 cm^{-1}. The relative intensities of these pairs did not change over the course of many experiments; therefore, the sidebands are not likely due to polymer.

N_2H_4 + HF. The new product absorptions noted above were seen only on codeposition of hydrazine and hydrogen fluoride samples; deposition of only one of the species did not produce these bands. Therefore, these absorptions must be due to a hydrazine–hydrogen fluoride complex. This is substantiated by the predictable behavior of these bands when DF was substituted for HF.

Comparison of the behavior of the new bands both under annealing and changes in reagent concentration allow separation into 1:1 and 1:2 complex categories. The 2928-, 940-, 922-, 1093-, 1043-, and 838-cm^{-1} bands all decreased in intensity in the same ratio upon annealing, while the 1966-cm^{-1} band increased. Also, as the Ar:HF ratio was decreased from 400:1 to 100:1, the relative intensity of the 1966-cm^{-1} peak grew substantially against the intensities of the other six peaks. It is therefore evident that the 1966-cm^{-1} band belongs to a higher order complex and is thus assigned to the 1:2 complex. The other absorptions, being less dependent on HF concentration, are attributed to the 1:1 complex.

Motions of the HF submolecule in the complex can be characterized as either the perturbed H–F stretching motion, ν_s, or one of the two H–F librational motions, ν_l(A) or ν_l(B), where A and B represent symmetric and antisymmetric motions with regard to the C_2 symmetry of the unperturbed hydrazine submolecule. The appropriate bands can be found by observing frequency shifts upon substitution of DF for HF; those bands due to HF will decrease by a predictable ratio. The following ratios were observed for three bands: 2928:2210 = 1.325; 940:723 = 1.300; 922:673 = 1.370. This supports assignment of the bands as ν_s, ν_l(B), and ν_l(A), respectively; further evidence for that assignment will be offered below.

Absorptions due to perturbed hydrazine submolecule modes include bands at 1094, 1043, and 838 cm^{-1}. These are assigned respectively to the symmetric NH_2 rock, $\nu_4{}^c$(A), the antisymmetric NH_2 wag, $\nu_{12}{}^c$(B), and the symmetric NH_2 wag, $\nu_6{}^c$(A).[2] All three modes are blue-shifted from their frequencies in unperturbed hydrazine (1086, 954, and 812 cm^{-1} in solid argon), which is the expected effect of hydrogen bonding on these types of motions. Other peaks identifiable as due to hydrazine, including ν_{11}, the antisymmetric NH_2 rock, as well as bands from various NH stretching motions in the 3400–3200-cm^{-1} range and bands in the 1600–1575-cm^{-1} range due to NH_2 scissors motions, either did not exhibit perturbed absorptions due to the 1:1 complex or were unresolvable from nearby hydrazine polymer or impurity bands.

Appearance of the DF counterparts of $\nu_{12}{}^c$ and $\nu_6{}^c$ at 1032 and 850 cm^{-1}, removed 11 and 12 cm^{-1} from their HF counterparts, suggests coupling of these modes with some other vibrational mode in the complex. Considering that the HF/DF ratios for the librational modes are slightly different from the more normal ammonia ratio (1.315),[8] one can deduce that coupling occurs between the librational and wagging modes in the hydrazine-HF complex. For example, coupling between ν_l(A) and $\nu_6{}^c$ pushes the wagging mode down to 838 cm^{-1} and the librational mode up to 922 cm^{-1}, which increases the HF:DF ratio to 1.370, slightly greater than the ammonia ratio of 1.315. When DF is substituted for HF, the coupling disappears as the librational mode shifts to 673 cm^{-1}, allowing $\nu_6{}^c$ to relax to 850 cm^{-1}. Similarly, $\nu_{12}{}^c$ and ν_l(B) interact, with the wagging motion increasing in frequency and the librational motion decreasing, explaining the lower HF:DF ratio (1.300). Again, with DF substitution, coupling is removed (ν_l(B) = 723 cm^{-1}) and the wagging motion can relax to lower frequency.

This coupling also serves as further evidence for the assignment of the librational modes as symmetric and antisymmetric with respect to the C_2 symmetry of the hydrazine molecule, which would otherwise be arbitrary. As only vibrational modes of the same symmetry can couple, this assignment is straightforward.

The structure of the 1:1 complex is comparable to that of the ammonia–HF complex,[8] with a hydrogen bond between the acidic hydrogen and the nitrogen lone pair. This can be seen by the blue shifts in the NH_2 wagging (ν_6 and ν_{12}) and rocking (ν_4) frequencies, which is typical of such a hydrogen bond. Also, the proximity of the hydrazine ν_s mode at 2928 cm^{-1} to that of ammonia at 3041 cm^{-1}, coupled with the electron-donating properties of the $-NH_2$ group compared to –H (which makes the nitrogen lone pair more basic and leads to a stronger hydrogen bond), supports this structure.

Consideration of the proton affinities of ammonia and hydrazine, however, indicates that the structure of the 1:1 complex may not be so simple. The PA difference between the two is on the order of 1–2 kcal/mol,[20,21] while the frequency difference between ν_s bands is 113 cm^{-1}. By a comparison with methylamine, NH_2CH_3, which supports a ν_s fundamental at 2816 cm^{-1} for the 1:1 complex with HF (225 cm^{-1} less than ammonia[12]) but has a proton affinity 10–12 kcal/mol greater,[20,21] it can be seen that the electron-donating properties of the $-NH_2$ group are not sufficiently strong to cause the observed apparent increase in basicity as reflected in the ν_s mode.

It is therefore postulated that there is a secondary, chelating hydrogen bond between the fluorine and a hydrogen atom on the

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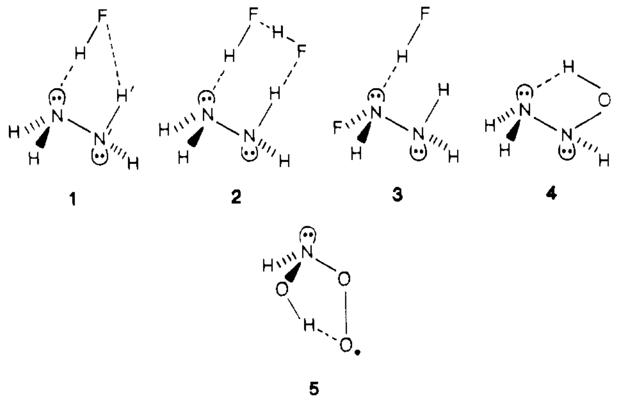
Chart I



opposite amine group from the one with the primary hydrogen bond (**1**; Chart I), to account for the extra perturbation of the HF stretching mode. This type of structure has been seen in the hydroxylamine–hydrogen fluoride 1:1 complex,[9] and the broad shape of the ν_s band in the N_2H_4 experiments is similar to that seen in the NH_2OH experiments, as opposed to the sharper peaks in the NH_3 and NH_2CH_3 experiments with HF.

The secondary hydrogen bond is feasible in terms of geometry, due to the skewed orientation of the NH_2 groups, which has the N–N′–H′ plane nearly coincident with the N′–N–(lone pair) plane. Since the N–N′ and N′–H bond lengths are comparable to the N–O and O–H bond lengths, respectively, in NH_2OH, hyrazine and hydroxylamine have essentially the same structures with respect to the formation of a 1:1 complex with an HF molecule. Thus, the structural considerations for hydroxylamine apply for hydrazine; i.e. a cyclic complex is reasonable.

Unfortunately, unlike hydroxylamine, there is little direct spectroscopic evidence in the hydrazine experiments to further support this model. The NH stretching bands are very weak, and no complex band could be seen in that region. The secondary hydrogen bond is not strong enough to significantly perturb the wagging motion of the "free" $N'H_2$ group; therefore, no complex bands are seen in that region either. Also, as for hydroxylamine, no perturbation of the torsional mode could be detected. This lack of evidence is not surprising, as the chelating hydrogen bond is at least as weak as its hydroxylamine counterpart, because of the slightly larger N–N′–H′ angle compared to N–O–H and the longer N–H bond length compared to O–H;[1] since the hydroxylamine secondary hydrogen bond is so weak that it only perturbs the OH stretching frequency 23 cm^{-1}, the energy of the secondary hydrogen bond for hydrazine must be quite small. However, the proton affinity and structural considerations mentioned above provide sufficient evidence to suggest the cyclic 1:1 structure.

A cyclic structure for the 1:2 complex (**2**) cannot be ruled out, although, as for hydroxylamine, little evidence for it was seen in the spectrum. The observed frequency for ν_{sa}, the stretching motion of the interior H_a–F molecule, at 1966 cm^{-1} is at a higher frequency than that for ammonia (1920 cm^{-1}), despite the greater basicity of the hydrazine lone pair. This suggests that some interaction between H_b–F and hydrazine could occur, to account for the decreased effect of H_b–F on ν_{sa}. Such an interaction has been suggested from ab initio calculations on the NH_3–$(NF)_2$ complex.[22] As no supplementary bands were seen, however, characterization of the 1:2 complex structure must remain uncertain.

N_2H_4 + F_2. The new bands appearing on codeposition of the two reagents must be due to a complex formed by reaction of the two species, as the bands did not appear on deposition of either reagent alone. All of the observed ands are assigned to the 1:1 combination of the two reagents, as they all behaved similarly on annealing, and all increased or decreased appropriately with changes in reagent concentration.

On the basis of the frequencies of these new bands, it is postulated that hydrazine and fluorine react to give the monofluorohydrazine–HF complex, N_2H_3F–HF (**3**), the hydrazine analogue of the product of the NH_3 + F_2 photolysis reaction, NH_2F–HF.[10] Comparison of this spectrum with that of N_2H_4 + HF shows the two to be similar, but with several important and expected differences. For example, due to the electron-withdrawing effect of the fluorine substituent, one would expect the nitrogen lone pair to be less basic than in hydrazine, with a corresponding decreased perturbation of ν_s, the HF stretching frequency. This is the case, as the ν_s band at 3113 cm^{-1} is of higher frequency than ν_s for the hydrazine–hydrogen fluoride complex (2928 cm^{-1}). The shift of 185 cm^{-1} is not as great as the difference between HF complexes of NH_3 and NH_2F ($\Delta\nu_s$ = 348 cm^{-1}), but as the fluorine electron-withdrawing effect in N_2H_3F is partially negated by the electron-donating properties of the NH_2 group, the smaller shift is expected.

Also, one would expect strong new bands corresponding to the wagging and rocking motions involving the NHF group and a small change of these frequencies for the NH_2 group compared to those for hydrazine. This is seen in the appearance of strong bands at 1282 and 1311 cm^{-1}, which are assigned respectively to the NHF rocking and wagging motions, perturbed by the HF ligand hydrogen bonded to the nitrogen lone pair. As for motions of the NH_2 group, the NH_2 rock shifts little (blue-shifted 5 cm^{-1} to 1091 cm^{-1}) and the wag is apparently coincident with the 954-cm^{-1} wag of hydrazine. This latter point strongly suggests HF attachment to the NHF group.

One would additionally expect to see a band corresponding to the NF stretching motion in the 900–1050-cm^{-1} region; however, there is only a weak band present at 1013 cm^{-1}, and this is weaker than expected for this motion. It is possible that this mode is obscured by either the 974-cm^{-1} ammonia or 954-cm^{-1} hydrazine absorption.

In some experiments a weak, broad band at 3044 cm^{-1} was seen; this is attributed to ν_s for a minor structure involving a secondary chelating hydrogen bond similar to the chelating hydrogen bond in the hydrazine–HF complex. This bond is very weak because of a larger N–N bond distance due to the electron-withdrawing effects of the fluorine substituent. Although there is ammonia impurity in the sample, the band is not due to the NH_3–HF complex, as no evidence for the very strong librational mode at 916 cm^{-1} was detected.

The weak bands at 726 and 680 cm^{-1} are assigned to ν_l, the librational modes of the HF submolecule in the 1:1 complex. These large shifts from the ν_l frequencies for the hydrazine–hydrogen fluoride complex are typical of the substitution of a fluorine atom for a hydrogen atom in the base submolecule.[10,23] Unfortunately, as experiments with hydrazine-d_4 were not done, DF shifts for these bands could not be observed.

There are two possible rotomers of NH_2NHF that could exist while the gauche configuration of hydrazine is maintained. The monofluorohydrazine spectrum does not yield any clues on the prevalence of either a hydrogen or fluorine atom opposite the nitrogen lone pair of the unsubstituted NH_2 group; however, one might expect electronic repulsions between the electron-rich fluorine and the lone pair to favor the structure shown in **3**.

The proposed mechanism for the reaction between hydrazine and fluorine to give the fluorohydrazine–hydrogen fluoride product is similar to that for the reaction between ammonia and fluorine to give NH_2F. Fluorine reacts to abstract a hydrogen atom from hydrazine and gives HF, $NH_2\dot{N}H$, and $F^•$; the radicals then combine, and the HF forms the hydrogen bond. Because the reaction occurs spontaneously, there is no opportunity to observe a hydrazine–fluorine complex band like the ammonia–fluorine complex;[10] however, the similar chemistry of hydrazine and ammonia allow a confident assumption of this radical mechanism.

The fact that hydrazine and fluorine reacted on deposition and did not require photolysis is indicative of the relative N–H bond dissociation energies in hydrazine and ammonia. The ammo-

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nia–fluorine reaction did not occur during sample deposition; photolysis was required. This suggests that the first N–H bond is more easily broken in hydrazine. Dissociation energy data show that this difference is on the order of 6–10 kcal mol^{-1},[1] which is due to stabilization of the $NH_2\dot{N}H$ radical by the electron-donating NH_2 group.

The lack of reaction on photolysis further indicates that the reagent pairs reacted on deposition; effective photolysis did take place as shown by the appearance of FO_2 bands on sample annealing.[24]

This is the first spectroscopic evidence for the existence of monofluorohydrazine as an intermediate in the reaction between hydrazine and fluorine; previous characterization had been hampered by the explosive reactivity of the two reagents.[1] Although the fluorohydrazine is complexed with hydrogen fluoride, experience with HF–amine complexes in this laboratory allow a prediction of the NH wagging mode at 1250 ± 20 cm^{-1} and the NHF rocking mode at 1280 ± 20 cm^{-1} for unperturbed N_2H_3F, which has not been characterized.

N_2H_4 + O_3. The chemistry between hydrazine and ozone is particularly rich, as seen by the three different classes of bands produced during the photolysis experiment. The most interesting of these classes is the one containing bands that appear on deposition but grow markedly on Hg arc photolysis (class I). On the basis of our experience with ozone photolysis experiments,[25,26] these bands can be assigned to the product of a 1:1 reaction between the two components.

The 1329-cm^{-1} band, which appears in a frequency region characteristic of NH bending motions, is assigned to the NH wagging motion of the photolysis product; however, the ^{18}O shift of 2 cm^{-1} indicates a small effect caused by the presence of an oxygen atom. This plus the significant blue-shift from the frequency of the relevant hydrazine mode suggests that one of the hydrogen atoms has been replaced with a group containing oxygen. On the basis of the photolysis reaction of NH_3 and O_3, which yielded NH_2OH,[27] a similar reaction is proposed for hydrazine and ozone:

$$NH_2NH_2 + O_3 \xrightarrow{(h\nu)} NH_2NHOH + O_2$$

This leads to assignment of the 1329-cm^{-1} band as the NH(OH) wagging motion, which allows for the small ^{18}O shift and the large blue-shift from the hydrazine wagging frequency.

The strong band at 1282 cm^{-1} is likewise assigned to a hydrogen motion, specifically the deformation of the NNH bond angle. There is no ^{18}O shift for this absorption, as would be expected. Also, this band shows a small blue-shift when compared to the NH_2 rock of hydrazine (1261 cm^{-1}), which may arise from repulsions with the added hydroxyl group.

Further support for the formation of hydroxyhydrazine comes from the appearance of the band at 3198 cm^{-1}, which corresponds to the OH stretching mode. This assignment is substantiated by a 7-cm^{-1} ^{18}O shift. Comparison of this frequency with the similar hydroxylamine frequency of 3635 cm^{-1} shows a significant red-shift, indicative of a hydrogen-bonding interaction involving the hydroxyl hydrogen. The intensity of the band rules out the possibility of its being due to a polymer, but the structure of the molecule allows the possibility of an internal hydrogen bond involving the lone pair on the NH_2 nitrogen atom (**4**). Rough calculations using the hydrazine r_{NN} and hydroxylamine r_{NO} and r_{OH} equilibrium bond distances and NNO and NOH bond angles of 101° give a hydrogen bond length of 1.95 Å. As bond lengths of 1.8 Å are common for the strongly hydrogen-bound base–HF complexes,[28] this result shows that the idea of an internal hydrogen bond for NH_2NHOH is reasonable.

The presence of this hydrogen bond suggests perturbation of the NH_2 wagging and rocking motions. Unfortunately, no appropriate band could be found for either mode. The 1282-cm^{-1} band could not be assigned to the wag because the 300+ cm^{-1} shift from the hydrazine wagging frequency was too great to be adequately rationalized, though the band showed an intensity more characteristic of a wag than a rock. It is possible that the frequencies of the modes were blue-shifted sufficiently to hide them under the intense ozone ν_3 band or under a hydrazine band.

Hydroxyhydrazine formation also suggests the appearance of NNO bond angle deformation and NO stretching bands. Considering the C_i symmetry of the molecule, these modes would certainly be mixed; the band at 734 cm^{-1} is therefore tentatively assigned to a mixture of these two motions, and possibly the NN stretching motion. This band is in the region of NO_2 bending motions; the NNO bend would be similar but lower in frequency for NH_2NHOH because of the extra hydrogen atoms involved in the motion. Presence of some NN stretching character balanches the effect of the NO stretch in terms of the ^{18}O shift, which is only 4 cm^{-1}. Other bands corresponding to different mixtures of these three modes could not be seen.

The other two bands in this class of photolysis products, which appear at 2910 and 2232 cm^{-1}, can only be assigned tentatively to an OH stretch of $(NH_2NHOH)-(N_2H_4)$ and a combination band, respectively. The 2910-cm^{-1} band corresponds to a 1:2 ozone–hydrazine product; the presence of polymer bands both at 1007 cm^{-1} and in the NH stretching region shows that hydrazine dimer was formed and that a 1:2 reaction is reasonable. Trapped by the matrix, the hydroxyhydrazine and hydrazine molecules would be forced to interact, and the extra 312-cm^{-1} shift indicates the strength of the intermolecular interaction as compared to the intramolecular interaction. As for the 2232-cm^{-1} band, it is likely to be a combination of the NNH bending motion described above and a typical NH_2 wagging motion.

The appearance of these bands on deposition and before photolysis is testimony to the high reactivity of the hydrazine molecule; of all the ozone matrix reactions studied in this laboratory, only that with trimethylphosphine took place before photolysis.[29] This also shows the relative weakness of the hydrazine NH bond compared with that of NH_3, as ammonia required photolysis to react with ozone to form NH_2OH. Bond dissociation energy values support this finding, since removal of the first hydrogen from hydrazine requires at least 6–10 kcal/mol less energy than for ammonia.[1]

Requiring 20 kcal/mol less energy to break than the hydrazine NH bond is the hydrazine NN bond.[1] One expects that additional products could be formed by breaking this bond, and it is to these products that the remaining two classes of photolysis products are attributed. However, identification proved to be difficult, as the bands seen did not match absorptions of any known molecule. Rejected as possible reactions were

$$\begin{aligned} NH_2NH_2 + O_3 \rightarrow\ & N_2H_2 + O_2 + H_2O \\ & H_2O_2 + N_2 + H_2O \\ & NO + NH_2O + H_2O \\ & NH_3 + HNO + O_2 \end{aligned}$$

because there was no evidence for the formation of diimide,[30] hydrogen peroxide,[31] nitrous oxide[32] (despite the apparent formation of water), or ammonia.[8]

Although the number of bands in each class are insufficient to make definitive statements about the structure of the products, they do offer some clues. For instance, of those bands which show a small growth on photolysis (class II), the 753-cm^{-1} band, characteristic of an NO_2 bend, displayed a sextet of bands when mixed oxygen isotope experiments are performed, indicating that there are three oxygen atoms in this molecule. Also, the 342-cm^{-1} band behaved like a torsional mode, shifting 3.5 cm^{-1} in $^{18}O_3$

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experiments, and the 3537-cm^{-1} band could be a hydrogen-bound OH stretch. A molecule that matches these characteristics is the radical **5**, which would be formed by breaking both the NH and NN bonds; however, this might be expected to be photosensitive and to be destroyed on photolysis.

Class III absorptions, which are destroyed on photolysis, include bands at 1438 and 1382 cm^{-1}, which became multiplets in mixed oxygen isotope experiments, and bands at 1525, 1517, and 535 cm^{-1}, which displayed no ^{18}O shifts. Possible products, involving only NN bond dissociation, are the peroxyamine and nitroxide radicals.

Conclusions

The infrared spectra of hydrazine and its reaction products with HF, F_2, and O_3 have been observed in an argon matrix. Vibrational assignments were made for hydrazine, resolving uncertainties in the assignments of the NH_2 wag (ν_6), the antisymmetric NH_2 scissors motion (ν_{10}), and the second harmonic of the torsion ($2\nu_7$).[2,6] Introducing HF into the matrix caused the formation of a hydrogen-bonded complex between the two reagents, involving a primary interaction between the nitrogen lone pair and the acid and a secondary interaction between a hydrogen atom on the adjacent amine group and the fluorine. This is similar to the chelated structure found for the NH_2OH–HF complex.[9]

Hydrazine and F_2 reacted on deposition to form the N_2H_3F–HF complex, which represents the first spectroscopic evidence for the monofluorohydrazine molecule. The fact that the reaction did not require photolysis corresponds with dissociation energy data[1] that show hydrazine to be more reactive than ammonia, which required photolysis to react with fluorine to give the NH_2F–HF complex.[10]

Hydrazine and O_3 reacted during condensation to give three sets of products, the major one being hydroxyhydrazine, NH_2NHOH. Evidence for an intramolecular hydrogen bond between the hydroxyl hydrogen and the lone pair on the α-nitrogen was seen from a large red-shift in the OH stretching frequency. Unlike most molecules, hydrazine did not require photolysis to react with ozone, demonstrating its high reactivity. As for N_2H_3F, this is the first evidence for NH_2NHOH.

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Registry No. N_2H_4, 302-01-2; NH_2NHF, 36336-10-4; NH_2NHOH, 112296-53-4; HF, 7664-39-3; F_2, 7782-41-4; O_3, 10028-15-6; $^{18}O_2$, 14797-71-8; D_2, 7782-39-0.

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Energy Redistribution and Localization in the Excited States of Ruthenium(II) Polypyridyl Complexes

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Excited-state absorption and resonance Raman spectra of the mixed-ligand complexes Ru(bpy)$_2$phen^{2+} (**1**) and Ru(bpy)$_2$DIP^{2+} (**2**) (DIP = 4,7-diphenylphenanthroline) are reported. The excited-state spectra of these mixed-ligand complexes show that the excited-state electron is localized on individual ligands but show nonstatistical contributions from states corresponding to each of the ligands present in the coordination sphere. On the basis of the excited-state absorption spectra, the bpy* contribution to **1*** is twice as much as that of phen*, whereas in case of **2*** the contribution of DIP* is much more than that of bpy*. Excitation of the mixed-ligand complexes at different wavelengths gave identical spectra, showing that the initial excited-state population relaxed quickly to an equilibrium mixture, which depends very much on the type of ligand. Intramolecular energy transfer is rapid. Excited-state absorption spectra of mixtures of parent tris chelates, in contrast, which depend upon the wavelength of excitation, show that intermolecular energy transfer is very slow. Excited-state localization and rapid relaxation to an equilibrium distribution is further supported by excited-state resonance Raman spectra of these mixed-ligand complexes. Vibrational transitions corresponding to bpy* dominate the spectrum of **1*** whereas the vibrational bands of DIP* dominate in case of **2***. Consistent with these results are the resonance Raman spectra of the excited states of the mixed-ligand complexes Ru(bpy)$_2$(4,4′-Ph$_2$-bpy)$^{2+}$ (**3**) and Ru(bpy)(4,4′-Ph$_2$-bpy)$_2$$^{2+}$ (**4**). These spectra clearly indicate preferential localization of excited-state energy on the 4,4′-Ph$_2$-bpy ligand. Thus, it may be possible to design systematically mixed-ligand complexes that would absorb light at a wavelength of choice but would funnel the energy onto a desired ligand.

The photophysics and excited-state redox properties of ruthenium complexes have received considerable attention due to the rich chemistry of their luminescent excited states.[1] Excited-state resonance Raman experiments show that the lowest excited state is a metal-to-ligand charge transfer (MLCT) state, and in the case of Ru(bpy)$_3$$^{2+}$, the excited-state electron is localized on one of the three bipyridyl ligands.[2] In mixed-ligand complexes of the type Ru(bpy)$_2$L^{2+}, two such states might be expected to be present: one, in which the excited-state electron is localized on the bpy ligand, and the other, in which the electron is localized on the second ligand L.[3,4] These states may exist in a rapid thermal equilibrium, leading to an effective averaging of the excited-state properties. Indeed the excited states of mixed complexes of Ru(II) with the ligands 2,2′-bipyridyl (bpy) and 1,10-phenanthroline (phen) show monoexponential decay in single-photon counting experiments,[4a] and the excited-state lifetimes of these mixed complexes are statistical averages of the parent tris chelates. These observations are consistent with several other excited-state

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