made to observe small intermolecular couplings in the C=C region with isotopic mixtures, but no new signal was found; it is therefore impossible to determine the relative orientation of the ethynyl group in the $Li(PA)_2$ sandwich.

Aside from the vibronic spectrum of free PA, two clearly separated electronic absorptions were observed for each product. The shorter wavelength bands (315-335 nm) are likely due to transitions to the higher energy levels of the ethynyl group because (i) no absorption was found in this region for LiC₆H₆ and (ii) these bands are 5 to 25 nm to the red of a vibronic progression $(1280\text{-cm}^{-1} \text{ interval with } 50\text{-cm}^{-1} h_2 \text{ to } d_2 \text{ shift})$ near 310 nm for Li plus C₂H₂ products.¹² It is significant that 568-nm radiation, which photolyzes PALi in the samples examined by infrared, destroys the 335-nm UV band with the larger red-shift, i.e., the species with the larger perturbation of the ethynyl group. The longer wavelength transitions (480–580 nm) probably originate from one of the filled E levels of the ring system interacting with Li 2p orbitals, since absorption bands were observed in this region for LiC₆H₆.¹²

Li + Styrene. The situation in the case of styrene is more difficult to extricate for two reasons: (i) the energy levels the most sensitive to complexation (C-H or C=C stretching modes, ring stretchings, and vinylic or ring deformation) are all crowding the same spectral regions, and (ii) it was not possible to carry out the same kind of selective photoconversions as with lithium-phenylacetylene isomers. For that reason we wish to stress that only the main bands pertaining to the Li-styrene isomers have been separated and assigned. A great deal of information might still be available provided that powerful monochromatic irradiations at 350 or 380 nm could be performed. With the help of selective deuteriation on the vinyl group, some conclusions can, however, be drawn. The first Li-monostyrene isomer (more stable upon near-UV excitation) is characterized by a set of modes almost insensitive to the vinyl deuteriation (1579 s, 1480 w, 1164 s), which can be confidently assigned to ring modes. These are very close to the position of the ring motions in the triple bond complex of Li-phenylacetylene. They denote little perturbation of the ring vibrational energy levels. On the other hand, the same complex is characterized by other bands showing definite sensitivity to vinyl deuteriation: strong bands at 1405 and 962 cm⁻¹ with styrene- d_3 and 1280 cm⁻¹ with the normal isotopes would match the position

of $\nu_{\rm CC} + \delta_{\rm CH_2}(\rm CD_2)$ energy levels for a C==C lithium complexation. It has been previously shown that the two C=C and CH_2 bond angle coordinates are strongly mixed in the normal modes of lithium-ethylene complexes and that they occur at 1390/1315 and 955/930 cm⁻¹ with C_2D_4 and 1290/1175 and 1510/1450 cm⁻¹ with C_2H_4 . This, in addition to the observation of a perturbed wagging mode at 718 cm⁻¹ (524 cm⁻¹ with styrene- d_3), facilitates documentation of vinyl group complexation. The second Limonostyrene isomer (less stable upon near-UV excitation) is characterized by reverse trends concerning the observed ring modes $(1460, 1447, 1325, and 957 \text{ cm}^{-1})$. These present large perturbations similar to the Li-benzene or arene complex of Liphenylacetylene and are therefore assigned to ν_8 , ν_{19a} , ν_{19b} , and ν_1 . One sharp band at 1557 cm⁻¹ having 87-cm⁻¹ d₃ shift is, however, to be assigned to $v_{C=C}$ of a slightly perturbed vinyl group. This mode has a 110-cm⁻¹ d_4 shift in ethylene and is assumed to have a roughly 70-cm⁻¹ d_3 shift in styrene⁹ (1631 to 1560 cm⁻¹) although coupling with the ν_8 ring stretching leads to a mixture in the normal coordinate. Hence, it seems likely that the second isomer corresponds to a structure with the lithium complexing the arene site.

Concerning the lithium-distyrene complex, the resemblance of its spectrum with that of the latter isomer of the monostyrene complex or with lithium-diphenylacetylene argues in favor of a diarene sandwich structure, but owing to the experimental difficulties in resolving all the product bands as well as because no experiment was performed with a mixture of styrene- d_5 and $-d_0$, this last question remains incompletely answered.

Conclusion

When CC triple or double bond and aromatic ring complexation sites coexist on the same ligand (phenylacetylene or styrene), Li atoms can complex to either π -system as deduced by matrix infrared spectra of the complexes. In the first case it is possible to convert the "ethynyl complexed" isomer into the more stable "ring complexed" structure by electronic excitation (red-yellow light) but electronic excitation of the latter (blue light) only achieves a partial reconversion. In the case of styrene, both isomers also coexist but no photoisomerization occurs upon visible light excitation. Both diphenylacetylene and distyrene complexes with lithium are observed and have structures comparable to the dibenzene species.

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Matrix Infrared Spectra and Normal-Coordinate Analysis of Isotopic Hydroxylamine Molecules

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Full arc photolysis of the NH_3-O_3 complex, formed by reagent codeposition with excess argon at 10–14 K, gave hydroxylamine as the sole product. Fundamental frequencies were obtained for hydroxylamine isotopes by using deuterium or ¹⁵N-enriched NH₃ or ¹⁸O-enriched O₃ precursors. Normal isotopic hydroxylamine and both fully and partially deuteriated hydroxylamine were also produced in high yields from the thermal decomposition of the tertiary hydroxylammonium phosphate salt, (NH₃OH)₃PO₄. All of the fundamentals except the NH₂ rock were observed for normal isotopic hydroxylamine. The experimental force field of hydroxylamine was constructed from the infrared data and it indicates that the unobserved NH₂ rock comes in the 1300-cm⁻¹ region as has been predicted by ab initio calculations.

Introduction

Hydroxylamine is a relatively simple but unstable molecule which has been known for a long time and can be prepared from thermal decomposition of the tertiary hydroxylammonium phosphate salt $(NH_3OH)_3PO_4$.¹ Hydroxylamine is particularly interesting because it is the simplest molecule with a different

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⁽¹¹⁾ To facilitate the comparisons, Wilson's benzene numbering has been kept concerning the ring motions, adding subscript a or b to designate the levels formerly degenerate in absence of substituents.

⁽¹²⁾ Manceron, L.; Andrews, L., unpublished results.

number of lone pairs on adjacent atoms.

Infrared spectra of NH₂OH in the vapor and in a Nujol mull were reported in 1952 by Giguère and Liu.² A little later Nightingale and Wagner measured infrared spectra of NH₂OH and ND₂OD in solid films.³ All of the fundamentals for NH₂OH except the NH₂ rock are known from these previous studies. There have also been further infrared studies of fine structure in the torsional band and the OH stretching band.^{4,5} Molecular orbital calculations on hydroxylamine predict that it has two minima in the torsional potential function corresponding to structures with NH₂ and OH groups either cis or trans.^{6,7} Furthermore, theoretical calculations suggest that the trans isomer is at least 6 kcal mol⁻¹ lower in energy than the cis.⁶⁻¹¹ The molecular structure of NH₂OH has been determined from the microwave spectrum, which characterized the trans conformation and found no evidence for the cis isomer.¹² Finally force constants of NH₂OH have been obtained from ab initio calculations^{13,14} and the NH₂ rock has been predicted at $1250 \pm 100 \text{ cm}^{-1}$ and 1451 cm^{-1} .

Formation of NH₂OH from mercury arc irradiation of the NH_3-O_3 complex provides a means of isotopically substituting each atomic position of NH2OH by using either deuterium or ¹⁵N-enriched NH₃ or ¹⁸O-enriched O₃ precursors. Therefore the present study was undertaken in order to obtain fundamental vibrational frequencies for NH2OH isotopes and to use these to construct the force field of NH2OH and to predict the fundamental frequency of the NH₂ rocking fundamental.

Experimental Section

Apparatus. The cryogenic refrigeration system and vacuum vessel have been described previously.¹⁵ Spectra were recorded with a Nicolet 7199 Fourier transform infrared spectrometer in the 4000–400-cm⁻¹ region. Argon matrices containing ozone and ammonia were irradiated for 30-min intervals with a BH-6 high-pressure arc lamp (1000 W, Illumination Industries, Inc.) in combination with a 10-cm water filter. Samples were exposed to either (A) 290-1000-nm radiation by means of a Pyrex filter which did not transmit the short-wavelength output of the mercury lamp or (B) the full arc output, 220-1000 nm.

Chemicals. Normal isotopic O_2 was obtained from Burdett, U. S. P. grade. Two samples enriched in ¹⁸O to 55% and 95%, respectively, were supplied by Yeda (Israel). NH₃ was supplied by Matheson (C. P. grade) and ND₃ (99% atom D) and $^{15}NH_3$ (99.8% ¹⁵N) were obtained from MSD Isotopes. The tertiary hydroxylammonium phosphate salt was supplied by Fluka A. G. and the deuteriated salt was prepared by refluxing (NH₃OH)₃PO₄ with D₂O and a trace of NaOH for several minutes.

Procedure. Ozone was generated by Tesla coil discharge of oxygen in a Pyrex tube immersed in liquid N2; residual O2 was removed by pumping at 77 K.16 Ozone and ammonia were diluted with argon and codeposited at 10-14 K through two separate spray-on lines at equal rates of 1.5 mmol h⁻¹ for 20 h. Matrix ratios of 200/1 or 300/1 were used for both Ar/O₃ and Ar/NH₃ gas mixtures. The samples were irradiated after deposition. Hydroxylamine was produced by heating the tertiary hydroxyl-

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Figure 1. Infrared spectra of a sample of $Ar/NH_3/{}^{16}O_3 = 600/1/2$ in the 400-4000-cm⁻¹ region (a) immediately after deposition at 16 K, and (b) after irradiation B. Hydroxylamine product bands are labeled H.

TABLE I: Absorbances of Product Bands after Irradiations A and B on an Argon Matrix Containing NH₃ and ¹⁶O₃

$\nu, \ \mathrm{cm}^{-1}$	А	В	ident
375.4	0.05	0.23	NH ₂ OH
895.9	0.005	0.04	NH ₂ OH
1117.4	0.07	0.34	NH ₂ OH
1349.8	0.03	0.10	NH ₂ OH
1597.0	0.01	0.04	NH ₂ OH
3289.7ª		0.01	NH ₂ OH
3333br ^a	0.03	0.04	\mathbf{D}^{b}
3634.7ª	0.04	0.14	NH ₂ OH

^a Measured from FTIR spectrum. The intensity was scaled accordingly. ${}^{b}D = NH_{2}OH - NH_{3}$ heterodimer.

ammonium phosphate salt to 30 °C in a glass tube while passing argon carrier gas over the sample.

Results

Preparation of hydroxylamine by photolysis of ammonia-ozone complexes and thermal decomposition of (NH₃OH)₃PO₄ will be described.

 $NH_3 + O_3$. Samples of ammonia (Ar/NH₃ = 300/1) and ozone $(Ar/O_3 = 300/1)$ were codeposited at 10 K for 12 h. The infrared spectrum recorded immediately after deposition is shown in Figure 1a. Doublets appearing at 707.1 and 708.1, 1047.6 and 1049.1, and 1109.6 and $\overline{1111.1}$ cm⁻¹ are due to ν_2 , ν_3 and ν_1 fundamentals, respectively, of ozone in the NH₃-O₃ complex and are blue-shifted from ν_2 , ν_3 , and ν_1 of isolated O₃ in solid argon. A strong band at 985.7 cm⁻¹ is due to ν_2 of ammonia in the NH₃-O₃ complex and is also blue-shifted from this mode in isolated NH₃. Exposure of the matrix to 290-1000-mm radiation decreased these NH₃-O₃ complex bands by 25% and produced new bands in the O-H, N-H, and N-O stretching and other regions; these new bands and intensities are listed in Table I. Subsequent exposure of the matrix to irradiation B decreased the NH_3 - O_3 complex bands by a further 60% and increased the product bands (see Table I). The infrared spectrum recorded after irradiation B is shown in Figure 1b. In view of the close similarity of these new bands with the infrared bands observed for NH₂OH, produced by thermal decomposition of (NH₃OH)₃PO₄ (see Table III), one can conclude that NH₂OH results from photodissociation of the NH₃-O₃ complex.¹

 $NH_3 + {}^{18}O_3$. Full arc irradiation of argon matrices containing NH_3 and ${}^{18}O_3$ (95% ${}^{18}O$) resulted in the appearance of bands due to ¹⁸O isotopically enriched hydroxylamine. All of the observed bands showed an ¹⁸O shift (see Table II); in particular the band in the O-H stretching region at 3634.7 cm⁻¹ shifted 11.5 cm⁻¹ to 3623.2 cm⁻¹ and the band in the N-O stretching region at 895.9 cm^{-1} shifted 20.6 cm^{-1} down to 875.3 cm^{-1} . The D band at 3333

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TABLE II: Comparison between Observed and Calculated Isotopic Frequencies (cm⁻¹) of NH₂OH

	NH	₂OH	NH ₂	¹⁸ OH	¹⁵ NH	I ₂ OH	¹⁵ NH	2 ¹⁸ OH	ND	2OD	ND ₂	¹⁸ OD	NH	₂ OD
vibratnl mode	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$\nu_1(OH)$ str	3634.7	3645.2	3623.2	3632.9	3634.7	3645.2	3623.2	3632.9	2683.6	2656.1	2668.4	2638.9		2656.4
$\nu_2(NH_2)$ s str	3289.7	3293.6	3289.7	3293.6	3284.1	3288.0	3284.1	3288.0	2412.9	2391.1		2391.1		3293.6
$\nu_3(\mathrm{NH}_2)$ sci	1598.9	1602.9	1596.3	1601.7	1596.6	1601.4		1600.1	1171.0	1161.5	1170.5	1160.3	1594.4	1590.5
$\nu_4(NOH)$ bend	1350.7	1352.0	1347.7	1349.0	1346.3	1348.1	1343.3	1345.0	1034.8	1016.8		1013.2		971.2
$\nu_5(\rm NH_2)$ wag	1117.0	1117.2	1111.1	1112.3	1114.7	1114.2	1108.8	1109.2	915.0	906.2	888.2	878.6	1144.7	1155.1
$\nu_6(NO)$ str	895.9	897.3	875.3	875.2	880.5	881.5	859.9	859.2	818.2	816.0	817.6	815.3	892.9	896.8
$\nu_7(\rm NH_2)$ a str	3353.3	3368.5		3368.5		3358.7		3358.7	2506.6	2485.5		2485.5		3368.5
$\nu_8(NH_2)$ rock		1311.4		1308.6		1308.7		1306.0		969.8		966.1		1311.4
v_9 torsion	375.9	376.2	374.7	375.2	375.0	376.0	374.4	375.1	277.3	273.0	276.2	271.7	313.2	309.1
	NH2	¹⁸ OD	ND	₂OH	ND_2	¹⁸ OH	NH	DOH	NHE	D ¹⁸ OH	NH	DOD	NHI	0 ¹⁸ OD
vibratnl mode	0bsd	calcd	ND obsd	2OH calcd	ND ₂ obsd	18OH calcd	0bsd	DOH calcd	NHE obsd	calcd	NH obsd	DOD calcd	NHI obsd	calcd
vibratnl mode $\nu_1(OH)$ str	0bsd	calcd 2639.1	ND obsd	2OH calcd 3645.2	ND ₂ obsd	¹⁸ OH calcd 3632.9	0bsd	DOH calcd 3645.2	NHE obsd	2 ¹⁸ OH calcd 3632.9	0bsd	DOD calcd 2656.3	NHI obsd	2639.0
vibratnl mode $\nu_1(OH)$ str $\nu_2(NH_2)$ s str	NH ₂ obsd	calcd 2639.1 3293.6	ND 	2OH calcd 3645.2 2391.5	ND ₂ obsd	¹⁸ OH calcd 3632.9 2391.5	0bsd	DOH calcd 3645.2 3332.9	NHE obsd	2 ¹⁸ OH calcd 3632.9 3332.9	Obsd	DOD calcd 2656.3 3332.9	NHI obsd	D ¹⁸ OD calcd 2639.0 3332.9
vibratnl mode $\nu_1(OH)$ str $\nu_2(NH_2)$ s str $\nu_3(NH_2)$ sci	<u>NH2</u> obsd	¹⁸ OD calcd 2639.1 3293.6 1589.9	<u>ND</u> obsd	2OH calcd 3645.2 2391.5 1148.0	Obsd	¹⁸ OH calcd 3632.9 2391.5 1147.8	<u>NH</u> obsd	DOH calcd 3645.2 3332.9 1474.4	<u>NHE</u> obsd 1460.7	2 ¹⁸ OH calcd 3632.9 3332.9 1472.1	<u>NH</u> obsd	DOD calcd 2656.3 3332.9 1450.7	NHI obsd	D ¹⁸ OD calcd 2639.0 3332.9 1449.5
vibratnl mode $\nu_1(OH)$ str $\nu_2(NH_2)$ s str $\nu_3(NH_2)$ sci $\nu_4(NOH)$ bend	<u>NH2</u> obsd	¹⁸ OD calcd 2639.1 3293.6 1589.9 965.8	ND obsd 1155.4 1368.4	2OH calcd 3645.2 2391.5 1148.0 1365.4	<u>ND</u> ₂ obsd	¹⁸ OH calcd 3632.9 2391.5 1147.8 1361.3	NH1 obsd 1462.5 1341.8	DOH calcd 3645.2 3332.9 1474.4 1331.4	NHE obsd 1460.7 1337.0	2 ¹⁸ OH calcd 3632.9 3332.9 1472.1 1328.9	NH obsd 1449.3 1020.2	DOD calcd 2656.3 3332.9 1450.7 1020.5	<u>NHI</u> obsd	2639.0 3332.9 1449.5 1016.2
vibratnl mode $\nu_1(OH)$ str $\nu_2(NH_2)$ s str $\nu_3(NH_2)$ sci $\nu_4(NOH)$ bend $\nu_5(NH_2)$ wag	<u>NH2</u> obsd 1593.6 1141.4	18OD calcd 2639.1 3293.6 1589.9 965.8 1151.4	ND obsd 1155.4 1368.4 836.9	2OH calcd 3645.2 2391.5 1148.0 1365.4 826.4	<u>ND</u> ₂ obsd	¹⁸ OH calcd 3632.9 2391.5 1147.8 1361.3 823.7	NH1 obsd 1462.5 1341.8 947.3	DOH calcd 3645.2 3332.9 1474.4 1331.4 936.4	NHE obsd 1460.7 1337.0 933.3	Calcd 3632.9 3332.9 1472.1 1328.9 925.1	NH obsd 1449.3 1020.2 934.9	DOD calcd 2656.3 3332.9 1450.7 1020.5 915.4	<u>NHI</u> obsd	2639.0 3332.9 1449.5 1016.2 899.0
vibratnl mode $\nu_1(OH)$ str $\nu_2(NH_2)$ s str $\nu_3(NH_2)$ sci $\nu_4(NOH)$ bend $\nu_5(NH_2)$ wag $\nu_6(NO)$ str	<u>NH2</u> obsd 1593.6 1141.4	¹⁸ OD calcd 2639.1 3293.6 1589.9 965.8 1151.4 874.6	ND obsd 1155.4 1368.4 836.9 918.9	20H calcd 3645.2 2391.5 1148.0 1365.4 826.4 917.3	<u>ND</u> ₂ obsd 1363.7	¹⁸ OH calcd 3632.9 2391.5 1147.8 1361.3 823.7 891.9	NH1 obsd 1462.5 1341.8 947.3 879.9	DOH calcd 3645.2 3332.9 1474.4 1331.4 936.4 883.0	NHE obsd 1460.7 1337.0 933.3	calcd 3632.9 3332.9 1472.1 1328.9 925.1 867.2	NH obsd 1449.3 1020.2 934.9 869.3	DOD calcd 2656.3 3332.9 1450.7 1020.5 915.4 877.7	NHI obsd	D ¹⁸ OD calcd 2639.0 3332.9 1449.5 1016.2 899.0 866.6
vibratnl mode $\nu_1(OH)$ str $\nu_2(NH_2)$ s str $\nu_3(NH_2)$ sci $\nu_4(NOH)$ bend $\nu_5(NH_2)$ wag $\nu_6(NO)$ str $\nu_7(NH_2)$ a str	<u>NH2</u> obsd 1593.6 1141.4	18OD calcd 2639.1 3293.6 1589.9 965.8 1151.4 874.6 3368.5	ND obsd 1155.4 1368.4 836.9 918.9	20H calcd 3645.2 2391.5 1148.0 1365.4 826.4 917.3 2485.5	<u>ND₂</u> obsd 1363.7	¹⁸ OH calcd 3632.9 2391.5 1147.8 1361.3 823.7 891.9 2485.5	NHI obsd 1462.5 1341.8 947.3 879.9	DOH calcd 3645.2 3332.9 1474.4 1331.4 936.4 883.0 2437.1	NHE obsd 1460.7 1337.0 933.3	calcd 3632.9 3332.9 1472.1 1328.9 925.1 867.2 2437.1	NH obsd 1449.3 1020.2 934.9 869.3	DOD calcd 2656.3 3332.9 1450.7 1020.5 915.4 877.7 2436.9	NHI obsd	D18OD calcd 2639.0 3332.9 1449.5 1016.2 899.0 866.6 2436.9
vibratnl mode $\nu_1(OH)$ str $\nu_2(NH_2)$ s str $\nu_3(NH_2)$ sci $\nu_4(NOH)$ bend $\nu_5(NH_2)$ wag $\nu_6(NO)$ str $\nu_7(NH_2)$ a str $\nu_8(NH_2)$ rock	<u>NH2</u> obsd 1593.6 1141.4	18OD calcd 2639.1 3293.6 1589.9 965.8 1151.4 874.6 3368.5 1308.6	ND obsd 1155.4 1368.4 836.9 918.9	20H calcd 3645.2 2391.5 1148.0 1365.4 826.4 917.3 2485.5 969.8	<u>ND₂</u> obsd 1363.7	¹⁸ OH calcd 3632.9 2391.5 1147.8 1361.3 823.7 891.9 2485.5 966.1	NHI obsd 1462.5 1341.8 947.3 879.9	DOH calcd 3645.2 3332.9 1474.4 1331.4 936.4 883.0 2437.1 1143.4	NHE obsd 1460.7 1337.0 933.3	calcd 3632.9 3332.9 1472.1 1328.9 925.1 867.2 2437.1 1140.2	NH obsd 1449.3 1020.2 934.9 869.3	DOD calcd 2656.3 3332.9 1450.7 1020.5 915.4 877.7 2436.9 1148.1	<u>NHI</u> obsd	2639.0 2639.0 3332.9 1449.5 1016.2 899.0 866.6 2436.9 1145.5

TABLE III:	Absorptions (cm ⁻¹) Appearing in Solid Argon on
Trapping the	Thermal Decomposition Products of (NH ₃ OH) ₃ PO ₄ and
(ND ₂ OD) ₂ P(),

(NH ₃ OH) ₃ PO ₄ ^a	(ND ₃ OD) ₃ PO ₄ ^b	ident ^c	
 374.0	277.3	NH ₂ OH	
402.5		agg	
410.2		agg	
727.1	541.8	NH ₂ OH	
735.7+	547.2	dimer	
896.2	915.1	NH2OH	
909.7		dimer	
974.1		NH ₃	
1117.6	818.2	NH ₂ OH	
1155.7+		dimer	
1351.4	1035.0	NH ₂ OH	
1469.0+		dimer	
1598.7	1171.6	NH ₂ OH	
2218.5	2218.5	N_2O	
2685.5		NH ₂ OH	
2948.2		NH ₂ OH	
3289.6	2412.9	NH ₂ OH	
3322.8		? -	
3339br+	2475	dimer	
3353.7	2506.6	NH ₂ OH	
3489.2-	2579.4	? -	
3635.2	2685.7	NH ₂ OH	
		-	

^aOn warm up to 30 K for 5 min, the bands labeled + increased, the band at 3489.2 cm⁻¹ labeled – disappeared and NH₂OH monomer bands decreased slightly. ^bThe deuterium counterpart of the 374.0-cm⁻¹ band came below the cutoff of the Nicolet spectrometer at 400 cm⁻¹. It appeared at 277.3 cm⁻¹ in the ND₃/¹⁶O₃ photolysis experiments. ^cAggregate bands include (NH₂OH)₂ and are denoted agg.

 cm^{-1} shifted 5 cm^{-1} to 3328 cm^{-1} .

 $^{15}NH_3 + O_3$. Irradiation of argon matrices containing $^{15}NH_3$ (99.8% ^{15}N) and O₃ resulted in the appearance of bands due to ^{15}N isotopically enriched hydroxylamine. In particular, the band in the N-H stretching region at 3289.7 cm⁻¹ shifted 5.6 cm⁻¹ to 3284.1 cm⁻¹ and the band in the N-O stretching region at 895.9 cm⁻¹ shifted to 880.5 cm⁻¹. These studies were repeated with $^{18}O_3$, and the product bands are compared in Table II.

 $ND_3 + O_3$. Photolysis of matrices containing ND₃ (99% atom D) and O₃ resulted in the appearance of bands due to deuterium substituted hydroxylamine (see Table II). The D band at 3333 cm⁻¹ shifted down to 2463.3 cm⁻¹. Similar experiments were done with ¹⁸O₃; the D band further shifted to 2449.3 cm⁻¹.

 NH_nD_{3-n} $(n = 0, 1, 2, 3) + O_3$. Full arc irradiation of argon matrices containing partially deuteriated NH₃ and O₃ resulted in the appearance of bands due to partially deuteriated hydroxylamine. A similar experiment was done with ¹⁸O₃.



Figure 2. (a, top) Infrared spectrum in the $400-4000 \cdot \text{cm}^{-1}$ region of a sample of Ar/NH₂OH prepared from thermal decomposition of (NH₃-OH)₃PO₄ at 30 °C. Hydroxylamine monomer and dimer bands are labeled H and D, respectively. (b, bottom) Infrared spectrum in the $400-4000 \cdot \text{cm}^{-1}$ region for a sample of Ar/ND₂OD prepared from thermal decomposition of (ND₃OD)₃PO₄. ND₂OD and (ND₂OD)₂ are labeled 6 and D, respectively.

 NH_2OH from Thermal Decomposition. A stream of argon was passed over $(NH_3OH)_3PO_4$ at 3 mmol h⁻¹ for 7 h; the infrared spectrum recorded immediately after deposition is shown in Figure 2a and peak locations of absorptions are listed in Table III. A similar experiment was run with the fully deuteriated tertiary hydroxylammonium phosphate salt, and the product bands observed in this experiment are shown in Figures 2b and 3 and listed in Table III. A third experiment was run with approximately 50% deuteriated salt; absorption frequencies of partially deuteriated hydroxylamine isotopes observed in this experiment have been incorporated into Table II. The band at 735.7 cm⁻¹ which shifted down to 547.2 cm⁻¹ on full deuteriation gave rise to a complex multiplet with components at 547.2, 551.1, 554.9, 560.5, 563.6,



Figure 3. Infrared spectrum in the 800-1500-cm⁻¹ region for a sample of deuteriated hydroxylamines prepared from the hydroxylammonium phosphate salt. Hydroxylamine isotopes are labeled as follows: 1, NH₂OH; 2, NHDOH; 3, ND₂OH; 4, NH₂OD; 5, NHDOD; 6, ND₂OD. Unidentified impurity bands are denoted by ?.



Figure 4. Infrared spectra of a sample of Ar/NH_xD_{3-x} (x = 0, 1, 2, 3)/¹⁶O₃ = 400/1/1 in the 250-400-cm⁻¹ torsional region (a) immediately after deposition at 16 K, and (b) after irradiation B.

683.9, 688.0, 722.9, 724.2, 730.0, and 735.7 cm⁻¹ on partial deuteriation. This multiplet did not decrease in intensity on warming to 30 K for 5 min unlike absorptions due to hydroxylamine monomer.

Discussion

Vibrational assignments will be considered for NH_2OH and a force constant analysis will be described.

 NH_2OH Assignments. None of the measured peak locations of NH_2OH formed by photolysis of the NH_3-O_3 complex in solid argon differed by more than 2 cm⁻¹ from those of NH_2OH formed by thermal decomposition of the tertiary hydroxylammonium phosphate salt and trapped in solid argon (compare Tables II and

TABLE IV: Observed and Predicted Fundamental Vibrational Frequencies (cm⁻¹) of NH₂OH

vibratnl mode	a	b	с	d	е	f	g
$\nu_1(O-H)$ str	3650	3634.7	4100	3892	3797	4126	3787
$\nu_2(NH_2)$ s str	3297	3289.7	3708	3626	3764	3718	3470
$\nu_3(NH_2)$ bend	1605	1598.9	1860	1654	1836	1855	1723
$\nu_4(\text{NOH})$ bend	1354	1350.7	1545	1462	1483	1556	1439
$\nu_5(\mathrm{NH}_2)$ wag	1115	1117.0	1289	1211	1125	1276	1200
$\nu_6(N-O)$ str	895	895.0	1155	1156	9 81	1276	957
$\nu_7(NH_2)a$ str	3350	3353.0	3792	3597	3823	3810	3585
$\nu_8(NH_2)$ rock		1311 ^h	1483	1451	1409	1482	1336
$\nu_9(NH_2OH)$ torsion	386	375.9	454	380	457	434	186

^aEarlier work, see ref 14. ^bArgon matrix: this work. ^cValues calculated by an ab initio Hartree-Fock SCF MO method using the 4-31G* basis set, ref 14. ^dValues calculated as for column c, but including the anharmonic constants, ref 14. ^eValues predicted by an ab initio MO calculation using the 4-31G basis set, ref 13. ^fValues predicted by an ab initio Hartree-Fock MO method using the 6-31G* basis set, ref 26. ^gValues predicted by an ab initio second-order Møller-Plesset method using the 6-31G* basis set, ref 26. ^hValue set timated from experimental force field in this work.

III). This indicates that the O_2 molecule, which is a byproduct of the photodissociation of the NH₃-O₃ complex, does not greatly perturb the NH₂OH molecule in the matrix cage.

All of the fundamentals of normal isotopic NH_2OH , apart from the NH_2 rock, have been previously assigned^{2-5,14} as detailed in column a of Table IV. These assignments are confirmed by the present new isotopic data.

The band at 3634.7 cm^{-1} in the O–H stretching region is clearly the O–H stretch of NH₂OH as it has an ¹⁸O shift of 11.5 cm⁻¹ and shifts down to 2683.6 cm^{-1} on deuteriation. The weak band in the N–H stretching region at 3289.7 cm^{-1} belongs to the symmetric NH₂ stretch which is predicted to show a ¹⁵N red shift of 5.3 cm⁻¹ (observed shift = 5.6 cm^{-1}) from the ratio of the diagonal G matrix elements for the symmetric NH₂ stretch taking a H–N–H bond angle of 107.1° (see later). The band at 895.9 cm⁻¹, which exhibits a 20.7 cm⁻¹ ¹⁸O and a 15.8 cm⁻¹ ¹⁵N shift, is due to the N–O stretch; a pure N–O harmonic oscillator would have a 23.6 cm⁻¹ ¹⁸O and a 16.0 cm⁻¹ ¹⁵N shift in this frequency region. The N–O stretching frequency of NH₂OH comes close to the 855 and 793 cm⁻¹ reported values for the N–O stretches of *cis*-HONO and *trans*-HONO, respectively, in nitrogen matrices.¹⁸

The band at 1598.7 cm⁻¹, which comes close to the NH₃ bend at 1638.9 cm⁻¹ in solid argon, belongs to the symmetric NH₂ bending mode. The intense absorption at 1117.0 cm⁻¹, which shifts down to 818.2 cm⁻¹ on full deuteriation, has an intermediate counterpart at 947.3 cm⁻¹ in the case of NHDOH. It is reasonable to assign this band to the NH₂ wag. The strong band in the low-frequency region at 375.9 cm⁻¹ shows very little ¹⁸O or ¹⁵N isotopic shift but has a large deuterium shift to 277.3 cm⁻¹ (H/D = 1.352). Furthermore, on partial deuteriation this band gives rise to a sextet having components at 277.3, 290.2, 313.2, 348.4, 358.1, and 375.9 cm^{-1} (see Figure 3). This band is clearly due to the torsional mode. The NH_2OH band at 375.9 cm⁻¹ is predicted to shift to 361.8 cm^{-1} for NHDOH (observed value = 358.1 cm^{-1}), 347.1 cm^{-1} for ND₂OH (observed = 348.4 cm^{-1}), 309.0 cm^{-1} for NH₂OD (observed = 313.2 cm⁻¹), 291.7 cm⁻¹ for NHDOD (observed = 290.2 cm⁻¹) and 273.2 cm⁻¹ for ND₂OD (observed = 277.3 cm^{-1}), calculated by taking ratios of diagonal G matrix elements of the torsions of NH₂OH isotopes and structural parameters reported in a previous microwave study.¹² There are two other bands associated with NH₂OH monomer, namely at 3353.3 and 1350.7 cm⁻¹. The band at 3353.3 cm⁻¹ in the N-H stretching region, which shifted down to 2506.6 cm⁻¹ on deuteriation, is due to the NH₂ antisymmetric stretch. Unfortunately, it was too weak to be observed with isotopically enriched ¹⁵N and ¹⁸O samples. The band at 1350.7 cm⁻¹, which shows an ¹⁸O shift of 3.0 cm⁻¹ and a ¹⁵N shift of 4.4 cm⁻¹ and

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which shifts down to 1034.8 cm⁻¹ on deuteriation (H/D = 1.305), is assigned to the N-O-H bend as it comes close to the N-O-H bend of N-methylhydroxylamine which has been reported at 1321 cm⁻¹.¹⁹ It is predicted to shift 7.1 cm⁻¹ with ¹⁸O and 1.2 cm⁻¹ with ¹⁵N from the diagonal G matrix elements. The poor agreement between the calculated and observed isotopic shifts is due to vibrational coupling of the N-O-H bend with other vibrational modes as is demonstrated in the normal-coordinate analysis (see later). The only unassigned fundamental of NH_2OH is the NH₂ rock, which was not observed presumably owing to low intensity. This is consistent with a small dipole moment change during the rocking motion since as one H-N-O angle opens the other one closes. The assignment of the NH₂ rocking vibration of a pyramidal amino group is often a difficult problem on account of its low intensity in the infrared. Finally, the weak band at 727.1 cm^{-1} is assigned to the overtone of the torsion of NH₂OH monomer. This mode has been observed in gas-phase studies⁴ at 751 cm^{-1} (the gas-phase torsional fundamental appears at 386 cm^{-1}).

Table II lists the measured infrared frequencies for all of the hydroxylamine isotopes observed either following mercury arc photolysis of the NH₃-O₃ complex or after the thermal decomposition of the tertiary hydroxylammonium phosphate salt. Bands due to NHDOH and NH₂OD isotopes were distinguished from bands due to the NHDOD and ND₂OH isotopes by varying the degree of deuteriation of the precursor. In this way the relative intensities of bands due to the two pairs of isotopes were altered. Bands due to NHDOH were distinguished from those due to NH₂OD by a comparison of the observed absorption frequencies with the calculated ones by using the force field obtained by a normal-coordinate analysis (see later); bands due to NHDOD were distinguished from those due to ND₂OH in a similar way.

 NH_2OH-NH_3 . The broad band at 3333 cm⁻¹ which was produced on mercury arc photolysis of the NH₃-O₃ complex and shifted to 3328 cm⁻¹ with ¹⁸O is assigned to the hydroxyl stretch of hydroxylamine hydrogen bonded to an ammonia molecule. This hydrogen-bonded hydroxyl group gave rise to absorptions at 2463.3 and 2449.3 cm⁻¹ in ND₃/ $^{16}O_3$ and ND₃/ $^{18}O_3$ experiments, respectively. A red shift of 300 cm⁻¹ is not unreasonable for a hydrogen-bonded O-H stretch; a shift of 180 cm⁻¹ was observed for the hydrogen-bonded O-H stretch of (H₂O)₂.²⁰ NH₂OH- NH_3 heterodimers are to be expected in these NH_3/O_3 experiments from photolysis of $(NH_3)_2$ -O₃ clusters. The assignment of this band was verified by codepositing Ar/NH₂OH and Ar/ NH₃ samples in a separate experiment, and a very intense, broad band was observed at 3333 cm⁻¹. No other bands were observed which could be attributed to NH₂OH-NH₃.

Hydroxylamine Dimer, $(NH_2OH)_2$. When Ar/NH₂OH matrices were formed by flowing argon carrier gas over heated $(NH_3OH)_3PO_4$, a broad band appeared in the infrared spectrum at 3340 cm⁻¹. This is due to the hydrogen-bonded O-H stretch of hydroxylamine dimer, (NH₂OH)₂, and is analogous to the hydrogen-bonded O-H stretch of NH₂OH-NH₃ discussed above. This band increased in intensity on warming to 30 K as did other bands at 735.7, 909.7, 1155.7, and 1469.0 cm⁻¹ which are also identified as belonging to $(NH_2OH)_2$ for this reason. The bands at 909.7, 1155.7, and 1469.0 cm⁻¹ are assigned to an N-O stretch, an NH₂ wag, and an N–O–H bending mode of $(NH_2OH)_2$. They are blue shifted by 13.0, 38.1, and 117.6 cm⁻¹, respectively, from their monomer modes. The red shift of 300 cm⁻¹ of the O-H stretch and the blue shift of 117.6 cm^{-1} in the N–O–H bend are indicative of a strong hydrogen-bonding interaction in $(NH_2OH)_2$. The band at 735.7 cm⁻¹, which also belongs to $(NH_2OH)_2$, shifted down to 547.2 cm⁻¹ on total deuteriation (H/D = 1.344), and on partial deuteriation, gave rise to a complex multiplet with 11 observed components. This dimer absorption at 735.7 cm⁻¹ does not lie close to any NH₂OH monomer fundamental, but the large deuterium shift suggests it is due to a motion with appreciable hydrogen character. As it comes close to the torsional overtone of NH₂OH monomer at 727.1 cm⁻¹ (see earlier), the band at 735.7

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Figure 5. Designation of internal coordinates of hydroxylamine. The geometry was taken from ref 12. $r_1 = r_2 = 1.016 \pm 0.008$ Å; R = 1.453 \pm 0.002 Å; $l = 0.962 \pm 0.005$ Å; $\alpha = 107.1 \pm 0.5^{\circ}$; $\beta_1 = \beta_2 = 103.25$ $\pm 0.5^{\circ}$; $\gamma = 101.37 \pm 0.5^{\circ}$. The angle between the NH₂ plane and the N-O bond was determined to be 67.3°.

 cm^{-1} can be assigned to the overtone of a torsion of $(NH_2OH)_2$ having an enhanced intensity relative to the overtone of the torsion of NH₂OH. The fact that as many as 11 components were observed on partial deuteriation supports this assignment since the maximum number of components in a multiplet of the monomer is six due to the torsion which provides evidence that this is an aggregate band.

The spectrum was carefully inspected for bands which might be due to the cis isomer of hydroxylamine. The only possibility was a weak band in the O-H stretching region at 3489.2 cm⁻¹ in experiments with the tertiary phosphate salt. This band which did not appear on photolysis of the NH₃-O₃ complex does not belong either to trans-NH2OH or (NH2OH)2 as it disappears on warming to 30 K. It had a counterpart at 2579.4 cm⁻¹ when the deuteriated tertiary hydroxylammonium phosphate salt was used. In the likelihood that the cis isomer is on the order of 6 kcal mol⁻¹ less stable than the trans isomer⁶⁻¹¹ a Boltzmann distribution at 300 K would contain approximately 10⁵ molecules of trans-NH₂OH for every molecule of cis-NH₂OH. Furthermore, there has been no evidence from recent microwave¹² or infrared studies^{4,5} of gas-phase NH₂OH to suggest that the cis isomer is present at room temperature. Although the possibility that the band at 3489.2 cm⁻¹ is the O-H stretch of cis-NH₂OH cannot be ruled out, it is more likely due to a byproduct of the thermal decomposition of $(NH_3OH)_3PO_4$. This contrasts PH_3/O_3 experiments where both cis- and trans-phosphinous acid, H₂POH, were produced in argon matrices by mercury arc photolysis of the PH₃-O₃ complex.²¹

Normal-Coordinate Analysis. The geometry of NH₂OH determined from microwave studies¹² was used in the normal-coordinate analysis. Nine internal coordinates are defined by changes in the structural parameters shown in Figure 5; the ninth coordinate, $\Delta \tau$, is defined as $(\Delta \theta(H^1 \text{NOH}) + \Delta \theta(H^2 \text{NOH}))/2$ where θ is the dihedral angle. The fundamental frequencies and best fit force constants were calculated by using the Wilson FG matrix method.²² At first, isotopes of C_s symmetry only were considered and the F and G matrices were factored into A' and A" symmetry blocks by using the following symmetry coordinates:

A /

A′	OH stretch	$S_1 = \Delta l$
	NH_2 symmetric stretch	$S_2 = (\Delta r_1 + \Delta r_2)/2^{1/2}$
	NH ₂ scissors	$S_3 = \Delta \alpha$
	NOH bend	$S_4 = \Delta \gamma$
	NH_2 wag	$S_5 = (\Delta\beta_1 + \Delta\beta_2)/2^{1/2}$
	NO stretch	$S_6 = \Delta R$
Α″	NH ₂ antisymmetric stretch	$S_7 = (\Delta r_1 - \Delta r_2) / 2^{1/2}$
	NH ₂ rock	$S_8 = (\Delta\beta_1 - \Delta\beta_2)/2^{1/2}$
	NH ₂ OH torsion	$S_9 = \Delta \tau$

A perturbation cycle was carried out for the A' symmetry block with the minimum number of interaction force constants in order

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A' block	OH str	NH ₂ s str	NH_2 bend	NOH bend	\mathbf{NH}_2 wag	NO str
\mathbf{S}_1	7.413 ± 0.018 (9.877)	(-0.022)	(-0.009)	(0.028)	(0.017)	(-0.004)
S_2		6.116 ± 0.034	(0.004)	(0.020)	(0.117)	(0.102)
S_3		(7.796)	(0.234) 0.563 ± 0.014	(0.038) -0.049 ± 0.009	(0.116) -0.051 ± 0.003	(0.123)
S_4			(0.815)	(-0.044) 0.912 ± 0.007	(-0.004) 0.100	(-0.033) 0.541 ± 0.077
S5				(1.116)	(0.101) 0.942 ± 0.020	(0.648) 0.731 ± 0.031
S_6					(1.160)	(0.676) 4.463 ± 0.152 (6.717)
	A" block	NH ₂ a st	T	NH ₂ rock	torsio	n
	S_7 6.153 ± 0.0 (7.796)		034	(0.030)	(-0.025)	
	S ₈	(7.750)		(0.030) 0.942 ± 0.020 (1.160)	(0.025)	
	S ₉			(1.100)	(-0.046) 0.0456 ± (0.0001

^a Units: Nm⁻¹ × 10⁻² for stretch-stretch, N rad⁻¹ × 10⁸ for stretch-bend, and Nm rad⁻² × 10¹⁸ for bend-bend. ^b Values in parentheses have been predicted by ab initio calculation using a 4-31G* basis set, ref 14. $^{\circ}F(NOH \text{ bend}, \text{NH}_2 \text{ wag})$ was constrained to $0.100 \times 10^2 \text{ Nm}^{-1}$ (see text).

to obtain the best fit to the observed frequencies.²³ Since the NH₂ rocking fundamental was not observed for any of the hydroxylamine isotopes of C_s symmetry, only the diagonal F matrix elements for the antisymmetric NH2 stretch and the torsion were determined for the A" symmetry block. The F and G matrices were then transformed into internal coordinates so that hydroxylamine isotopes of less than C_s symmetry could be included in the calculations. Table II compares measured and calculated frequencies for NH₂OH and all of its isotopes. There is good agreement between these sets of values considering that the frequencies were assumed to be harmonic. The best fit force constants are given in symmetry coordinates in Table V.

The off-diagonal force constant for the NOH bend and NH₂ wag was constrained at 0.100×10^{-18} Nm rad⁻², similar to the value of 0.101×10^{-18} Nm rad⁻² predicted by the theoretical study.¹⁴ This was necessary in order to try to reproduce the blue shift of the N-O-H bending frequency of ND₂OH (observed N-O-H bending frequency = 1368.4 cm^{-1}) relative to that of NH_2OH (1350.7 cm⁻¹). As can be seen from Table II, the calculated blue shift was 13.4 cm⁻¹ compared to an observed value of 17.7 cm⁻¹.

The off-diagonal force constant belonging to the H-N-O bends was constrained at various values in the range -0.05 < F(HN-O,HNO < 0.05 × 10⁻¹⁸ Nm rad⁻². Sets of force constants were found giving an equally good fit of calculated to observed frequencies in each case, but of course, the calculated fundamental frequency of the NH₂ rock was very sensitive to F(H-N-O,H-N-O). Although it was not possible to arrive at a very precise value of F(HNO,HNO) from the infrared data of this work, its value was constrained to zero as it is likely to be small for two reasons. Firstly, it was predicted to be zero by the theoretical calculations using a 4-31G* basis set, and it changed sign when calculated by STO-3G and 4-31G basis sets.^{13,14} Secondly, the analogous off-diagonal force constant belonging to the H-N-C bends of methylamine, CH₃NH₂, was found to be only -0.007 \times 10⁻¹⁸ Nm rad⁻² in a previous matrix infrared study.²⁴

Interaction force constants not listed in the A' symmetry block appear to be appreciably less important than those which have been entered. Force constants predicted for hydroxylamine from ab initio MO calculations using a 4-31G* basis set¹⁴ have been entered in Table V for comparison with the experimental values here. As can be seen from Table V, the diagonal F matrix elements from ab initio calculations are greater than the experimental

values as is expected for theoretically derived values. The most important off-diagonal terms are due to the NO stretch/NH₂ wag and the NO stretch/NOH bend interactions as predicted.¹⁴ Also, the signs of the interaction force constants are in agreement with the theoretical study. Off-diagonal elements are estimated by ab initio calculation with the same precision as that for diagonal elements unlike experimentally determined off-diagonal F matrix elements, which are often hard to estimate even for small molecules. Finally, the value of 0.563 (±0.020) \times 10^{-18} Nm rad $^{-2}$ for the diagonal force constant of the NH₂ scissors can be compared with a value of 0.59 (\pm 0.07) × 10⁻¹⁸ Nm rad⁻² for this force constant in free ammonia.25

(0.070)

Assignment of a perpendicular type band at 750 cm⁻¹ to the NH₂ rock of gas-phase² NH₂OH was later shown to be erroneous since this band belongs to the first overtone of the torsional vibration.⁴ In fact the NH₂ rock remains unobserved to date owing to low intensity. Fundamental frequencies of normal isotopic NH₂OH predicted by ab initio calculations^{13,14,26} are given in Table IV and, as can be seen from the table, the calculated frequencies are in fairly good agreement. Such predictions need to be scaled in order to correct both for deficiencies in the theory and for the neglect of anharmonicity. Accordingly the ab initio studies predict the NH₂ rock of NH₂OH to appear in the 1300-cm⁻¹ region. The frequency of the NH_2 rock was estimated by using the diagonal and off-diagonal force constants of the H-N-O bending modes. The latter was constrained to zero by comparison with the recent theoretical study,¹⁴ as previously mentioned.

The value of 1311.4 cm⁻¹ estimated for the NH₂ rock of NH_2OH in this work comes in the same region as one of the NH_2 rocking frequencies of N_2H_4 which has been reported at 1275 cm⁻¹ in the gas-phase²⁷ (1261 cm⁻¹ in solid argon²⁸). Additionally, ethylamine has two weak absorption bands at 1294.0 and 1238.4 cm⁻¹ in the gas phase.²⁹ Both bands show ¹⁵N isotope shifts of 1.5 cm^{-1} which is consistent with their assignment to coupled NH₂ and CH₂ twisting vibrations. Also, the ND₂ rock of deuteriated nitramide, ND₂NO₂, in solid argon at 12 K has been reported at 972 cm⁻¹, 30 close to the value of 969.8 cm⁻¹ calculated for the ND₂ rock of ND₂OD in this work. The NH₂ rock of NH₂NO₂ was

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reported at 1226.7 cm⁻¹, apparently interacting strongly with the NO₂ antisymmetric stretch. The closest infrared band to the frequency calculated for the rock in this work was a weak feature at 1287 cm⁻¹. Unfortunately no isotopic data exists for this band.

Mechanism. The NH₃-O₃ complex photodissociated with near-ultraviolet irradiation at a wavelength threshold¹⁷ of 380 nm suggesting a weak electronic interaction between NH₃ and O₃ in the complex. This contrasts the Me₃N-O₃ complex which photodissociated with red light ($\lambda > 590$ nm) and with the F₃N-O₃ complex which required full arc irradiation for photodissociation.³¹ These experimental wavelength threshold values appear to bear an inverse relationship with the ionization potentials of the donor in the ozone complex. The NH₃-O₃ complex probably gives way to an excited amine oxide intermediate following O atom transfer from O₃ to NH₃. NH₂OH is formed from this intermediate via a 1,2 H-atom migration.

$$H_3N-O_3 \xrightarrow{n\nu} [H_3N-O]^* + O_2 \xrightarrow{} H_2NOH + O_2$$

In similar experiments with trimethylamine, trimethylamine oxide (Me₃NO) was observed as a stable photoproduct³¹ since a similar H-atom migration is not possible. Another possible product, HNO,³² was not observed in these experiments contrasting the observation of HPO from photolysis of the PH₃–O₃ complex.²¹ In similar experiments with NF₃, however, FNO was the only product observed.³¹ It was characterized by a band at 506.8 and doublets at 744.8, 749.7, 1851.2, and 1856.4 cm⁻¹, which shifted to 498.0 and 736.5, 741.3, 1802.6, and 1807.7 cm⁻¹ with ¹⁸O. These are in good agreement with 511, 751, and 1851 cm⁻¹ values

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previously observed for FNO in solid argon.³³ Trifluoramine oxide, F_3NO ,³⁴ was not observed.

Conclusions

Near-ultraviolet photolysis of the NH₃–O₃ complex in solid argon gave NH₂OH as the sole photoproduct. This observation is in marked contrast to similar experiments where the PH₃–O₃ complex was dissociated by red visible radiation and H₃PO, HPO, H(HO)₂PO, and H₂POH, the phosphorus analogue of hydroxylamine, were observed as primary photoproducts.²¹ NH₂OH and its deuteriated isotopes were also formed in high yield from the thermal decomposition of the tertiary hydroxylammonium phosphate salt. An experimental force field has been obtained for hydroxylamine by means of a least-squares fit of the observed fundamental frequencies of hydroxylamine isotopes to calculated values using the Schachtschneider force constant adjustment program.²³ This force field shows good agreement with that predicted by ab initio calculations¹⁴ and predicts the NH₂ rock for NH₂OH in the 1300-cm⁻¹ region.

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Registry No. NH₂OH, 7803-49-8; NH₂¹⁸OH, 113321-72-5; ¹⁵NH₂OH, 72960-76-0; ¹⁵NH₂¹⁸OH, 113321-73-6; ND₂OD, 16355-70-7; ND₂¹⁸OD, 113321-74-7; NH₂OD, 36722-24-4; ND₂OH, 36722-26-6; NO₂¹⁸OH, 113321-75-8; NHDOH, 36722-25-5; NHD¹⁸OH, 113321-76-9; NHDOD, 36722-27-7; NHD¹⁸OD, 113321-77-0; NH₃-O₃ complex, 60951-77-1; (NH₃OH)₃PO₄, 20845-01-6.

Bis(ethylene)gold(0) and Bis(propylene)gold(0) Complexes: Gold Nuclear Hyperfine and Quadrupole Coupling Tensors

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Electron spin resonance spectra of bis(ethylene)gold(0) and bis(propylene)gold(0) complexes generated in argon matrices have anomalous hyperfine splitting patterns (quartets with a smaller inner spacing, and a doublet pattern). The anomaly is shown to arise from a ¹⁹⁷Au nuclear quadrupole coupling tensor of extreme asymmetry. The g tensor and the ¹⁹⁷Au hyperfine and quadrupole coupling tensors of bis(ethylene)gold(0) were determined as follows: $g_z = 2.1791$ (6), $g_x = 1.9833$ (6), $g_y = 1.8498$ (6); $A_z = -98$ (3), $A_x = -55$ (3), $A_y = -114$ (3) MHz; and $P_z = -93$ (20), $P_x = -3$ (1), $P_y = +96$ (20) MHz. The corresponding parameters of bis(propylene)gold(0) were also determined.

Introduction

Recently we reported on ESR studies of mono- and bis-(ethylene) complexes of Au(0) and the analogous propylene complexes.^{1,2} The complexes were generated by cocondensation of the gold atoms and ethylene or propylene molecules in argon matrices at near liquid helium temperature. The ESR spectra of Au(0)-monoethylene and Au(0)-monopropylene are characterized by an extremely large, essentially isotropic hf (hyperfine) coupling tensor of the ¹⁹⁷Au nucleus (natural abundance = 100%, $I = {}^{3}/_{2}$, $\mu = 0.1439\beta_{n}$). The ESR spectra of bis(ethylene)gold(0) and bis(propylene)gold(0) are, on the other hand, characterized by an orthorhombic g tensor of large anisotropy and a relatively small but highly anisotropic ¹⁹⁷Au hf coupling tensor.

The structure of bis(ethylene)gold(0) and bis(propylene)gold(0) was concluded to be

The complex is thus formed by the dative mode of the π_y electrons of the ligands into the vacant Au 6s and 6p_y orbitals and the back-donation from the semifilled Au 6p_x orbital into the antibonding π_y^* orbitals of the ligands.

In an LĆAO-MO description the semifilled orbital of the above complex comprises only the carbon $2p_y$ orbitals and the Au $6p_x$ orbital. The small but highly anisotropic ¹⁹⁷Au hf tensor is hence accounted for, and the orthorhombic **g** tensor of large anisotropy is due to the large spin-orbit coupling constant of the Au atom and closely lying filled and vacant orbitals involving the Au $6p_y$ and $6p_z$ orbitals, respectively.

Figure 1 shows the bis(ethylene)gold(0) region of the ESR spectrum observed from the Au/C_2H_4 (10%)/Ar system. The bis(ethylene)gold(0) signals are indicated by arrows marking the positions of the principal g values of the complex. Identification

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