Matrix Reactions of Germane and Oxygen Atoms. Infrared Spectroscopic Evidence for Germylene–Water Complex, Germanone, Germanol, Hydroxygermylene, and Germanic Acid

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An extensive infrared study of the photochemical reaction of germane and ozone has been performed in solid argon. Isotopic substitution at all positions and filtered photolysis provide a basis for identification of seven new molecular product species. Germanone (H_2GeO), the germylene–water complex (H_2O–GeH_2), and hydroxygermylene (HGeOH) appeared on red photolysis and gave way to germanic acid ($(HO)_2GeO$), its peroxo isomer ($H(O_2)GeOH$), germanium oxide (GeO), and germanol (H_3GeOH) with ultraviolet photolysis.

Introduction

A previous study of the matrix reactions of silane and oxygen atoms provided infrared spectroscopic evidence for the silanol, silanone, and silanoic and silicic acid molecules,[1] which are the silicon-containing analogues of the well-known small organic molecules methanol, formaldehyde, and formic and carbonic acids, respectively. Of these novel molecules, silanone and silanoic and silicic acids contain silicon–oxygen double bonds, which are of considerable current interest. The present study was undertaken in order to produce and characterize novel species containing germanium–oxygen linkages. In particular, it was believed that new species with germanium–oxygen double bonds would be likely products. Such species are probably reactive as theoretical studies suggest that multiple bonds to germanium are less favorable than for Si and much less favorable than for C.[2,3] Nevertheless, GeO[4,5] and F_2GeO[6] have been observed in low-temperature matrices and dialkylgermanones have also been produced as transient species.[7,8] The technique of low-temperature matrix isolation employed in this study is particularly useful for the formation and trapping of such reactive species.

Experimental Section

Apparatus. The cryogenic refrigeration system and vacuum vessel have been described elsewhere.[9] Spectra were recorded on a Perkin-Elmer 983 grating spectrophotometer over the range 4000–180 cm^{-1} and on a Nicolet 7199 FTIR spectrometer over the frequency region 4000–400 cm^{-1} at a spectral resolution of 0.24 cm^{-1} and frequency accuracy of 0.1 cm^{-1}. Samples were irradiated for 1.0-h intervals at progressively shorter wavelengths with a high-pressure mercury arc lamp in combination with a quartz focusing lens, Corning glass and 10-cm water filters, which exposed the samples to the following wavelength ranges: (A) 590–1000 nm; (B) 380–1000 nm; (C) 290–1000 nm; and (D) full arc (220–1000 nm).

Chemicals. Ozone was generated by Tesla coil discharge of oxygen in a Pyrex tube and condensed with liquid N_2; residual O_2 was removed by pumping.[10] Normal isotopic O_2 was obtained from Matheson (lecture bottle). Two samples enriched in ^{18}O to 55% and 98%, respectively, were supplied by Yeda (Israel). GeH_4 (Matheson) was used directly, and GeD_4 was prepared as follows. $GeCl_4$ and D_2O were reacted in a 500-mL round bottom flask fitted with a thermometer, an addition funnel, and a dry ice condenser, thus forming GeO_2 (8.57 mmol) and DCl (1 M) in situ. A solution of $NaBD_4$ in D_2O (12.0 mmol) was slowly added to the GeO_2 slurry with the condenser cooled by a dry ice/acetone slush. The deuteriated germane product was passed through four traps cooled to −196 °C. The deuterium enrichment was greater than 95% by comparison of the Ge–H and Ge–D stretches in the product matrix infrared spectrum. A partially deuteriated germane mixture GeH_4–D_x (x = 0–4) was synthesized by the same method using partially deuteriated water and a mixture of $NaBH_4$ and $NaBD_4$.

Procedure. Ozone and germane were diluted with argon and codeposited from two separate manifolds at equal rates of 1.5 mmol/h for 10 h onto a CsI substrate. Samples were photolyzed after deposition, and additional spectra were recorded.

Results

$GeH_4 + O_3$. Samples of germane (Ar/GeH_4 = 200) and ozone (Ar/O_3) = 150) were codeposited at 14–18 K for 10 h, and the infrared spectrum showed absorptions due to the precursors GeH_4 and O_3.[10,11] Exposure of the matrix to radiations A and B produced a number of bands which are listed in Table I. Subsequent exposure of the matrix to radiations C and D produced changes in the intensities of the product bands as detailed in Table I. Bands have been grouped into categories according to their photochemical behavior in these four wavelength regions: group 1, produced by irradiation A, increased 4 times on irradiation B, destroyed by irradiation C; group 2, produced by irradiation A, increased 2.5 times on irradiation B, destroyed by irradiation C; group 3, produced by irradiation A, increased 3 times on irradiation B, unaffected by irradiation C, slight decrease on irradiation D; group 4, produced by irradiation B, increased 10 times on irradiation C, no change on irradiation D; group 5, produced by irradiation B, increased 10 times on irradiation C, increased 1.1 times on irradiation D; group 6, produced by irradiation B, increased 2.5 times on irradiation C, increased 1.1 times on irradiation D. Bands of each group are due to different product species. Absorptions of particular importance appeared in the O–H stretching region (Figure 1), in the Ge–H stretching region (Figure 2), in the Ge=O stretching region (Figure 3), and in the Ge–O stretching region (Figure 4).

$GeH_4 + {}^{18}O_3$. The four new bands at 3597.4, 3630.7, 3652.0, and 3686.9 cm^{-1} in the O–H stretching region were shifted to

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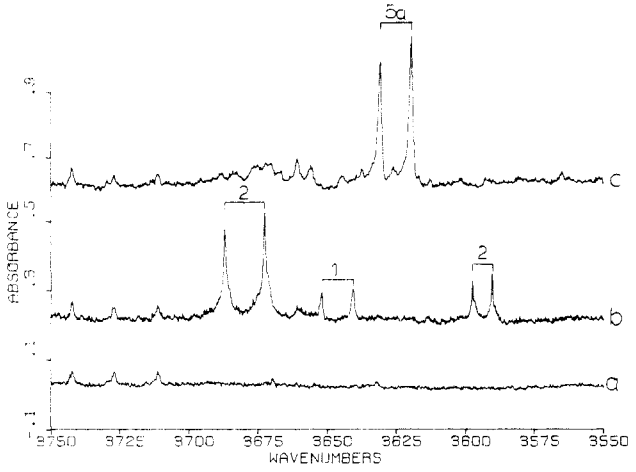


Figure 1. Infrared spectra of a sample of $Ar/GeH_4/^{16}O_3$ = 1200/3/4 in the 3550–3750-cm^{-1} O–H stretching region (a) immediately after deposition at 14–18 K, (b) after irradiation B, and (c) after irradiation D.

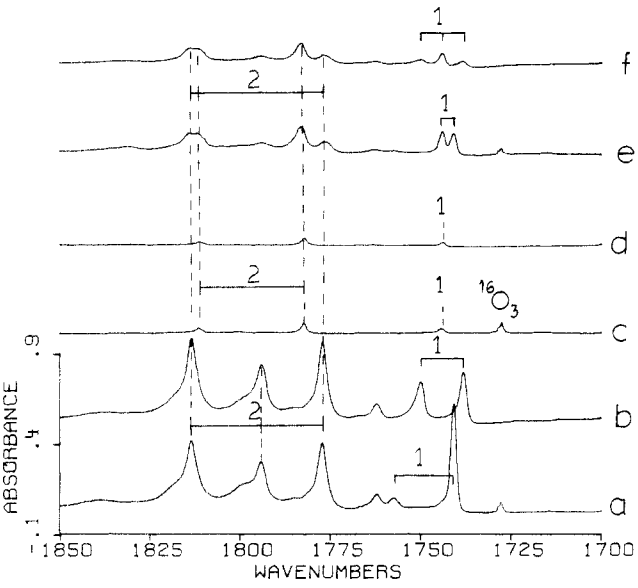


Figure 2. Infrared spectra in the 1700–1850-cm^{-1} Ge–H stretching region after irradiation B on (a) $Ar/GeH_4/^{16}O_3$, (b) $Ar/GeH_4/^{18}O_3$, (c) $Ar/GeD_4/^{16}O_3$, (d) $Ar/GeD_4/^{18}O_3$, (e) $Ar/GeH_xD_{4-x}/^{16}O_3$, and (f) $Ar/GeH_xD_{4-x}/^{18}O_3$ samples. All argon/germane/ozone ratios were 1200/3/4.

3590.3, 3619.5, 3640.6, and 3672.5 cm^{-1}, respectively, with oxygen substitution. In the Ge=O stretching region, the strong triplet belonging to group 5 with components at 971.4, 972.6, and 974.5 cm^{-1} gave way to a strong absorption at 963.9 cm^{-1} and a quintet having components at 912.8, 915.3, 916.5, 917.7, and 920.0 cm^{-1}, which can be seen in Figure 4b. In addition, a triplet belonging to group 5 with components at 925.3, 927.9, and 930.5 cm^{-1} is also present in Figure 4b. The three triplets due to group 1, 5a, and 6 absorptions and the quartet (species **5a**), which appeared in the Ge–O stretching region, all showed large ^{18}O shifts as detailed in Table II.

GeH_4 + $^{16,18}O_3$. The most common multiplet in this experiment was a doublet with equal intensity components centered on the pure $^{16}O_3$ and $^{18}O_3$ peak locations. For example, Figure 1 shows four such doublets in the O–H stretching region. In the Ge=O stretching region a species **5a** band, which was not present in pure $^{16}O_3$ or $^{18}O_3$ experiments, appeared at 966.9 cm^{-1}. This band came between the triplet at 971.4, 972.6, and 974.5 cm^{-1} (in $^{16}O_3$ experiments) and the strong band at 963.9 cm^{-1} (in $^{18}O_3$ experiments), and was approximately twice as intense as the latter band. In the Ge–O stretching region a sextet due to species **5a** was observed with components at 739.9, 740.7, 741.6, 742.3, 743.7, and 744.3 cm^{-1}. This sextet, which was not present in pure $^{16}O_3$ or $^{18}O_3$ experiments, came between the species **5a** quartet with components at 747.1, 749.1, 751.3, and 753.5 cm^{-1} (in $^{16}O_3$ experiments) and the triplet at 716.8, 718.8, and 721.0 cm^{-1} (in $^{18}O_3$ experiments). A multiplet, due to mixed $^{16,18}O_3$ counterparts of the species **4** triplet at 638.2, 639.7, and 641.3 cm^{-1}, was not observed presumably because it was too weak on account of isotopic dilution.

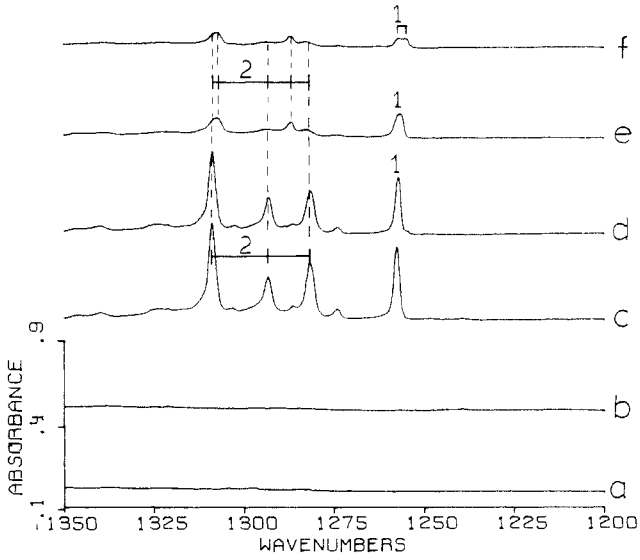


Figure 3. Infrared spectra in the 1200–1350-cm^{-1} Ge–D stretching region after irradiation B on (a) $Ar/GeH_4/^{16}O_3$, (b) $Ar/GeH_4/^{18}O_3$, (c) $Ar/GeD_4/^{16}O_3$, (d) $Ar/GeD_4/^{18}O_3$, (e) $Ar/GeH_xD_{4-x}/^{16}O_3$, and (f) $Ar/GeH_xD_{4-x}/^{18}O_3$ samples. All argon/germane/ozone ratios were 1200/3/4.

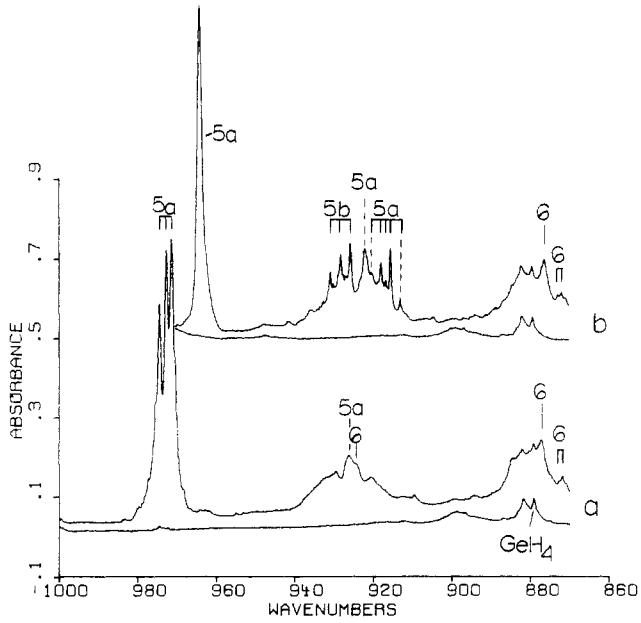


Figure 4. Infrared spectra in the 860–1000-cm^{-1} "Ge=O" stretching region of (a) $Ar/GeH_4/^{16}O_3$ = 1200/3/4 immediately after deposition and irradiation D, and (b) same for $Ar/GeH_4/^{18}O_3$.

GeD_4 + $^{16}O_3$. The infrared spectrum after codeposition of GeD_4 and $^{16}O_3$ indicated approximately 5% $GeHD_3$ impurity. The bands in the O–D stretching region at 2677.5 (species **5a**) and 2695.1 cm^{-1} (species **1**) bear similar H/D ratios of 1.356 and 1.355, respectively, with their protonated counterparts. The species **2** bands in the O–D stretching region at 2627.8 and 2738.5 cm^{-1} exhibited different H/D ratios of 1.369 and 1.346, however. In the Ge–D stretching region (see Figure 3), bands belonging to species **2** appeared at 1281.6, 1293.3, and 1308.9 cm^{-1} with H/D ratios of 1.387, 1.388, and 1.386, respectively. In addition, a band at 1257.6 cm^{-1} due to species **1** exhibited an H/D ratio of 1.385. Other important bands in this region were a species **3** band at

TABLE I: Absorbances of Product Bands Produced by Irradiation[a] of an Argon Matrix Containing GeH_4 and $^{16}O_3$

ν, cm^{-1}	A	B	C	D	indent
396.9		0.045	0.44	0.50	**5a**
421.5		0.01	0.10	0.12	?
466.0			0.025	0.025	?
565.0	0.03	0.08			**1**
638.2			0.04	0.04	**4**
639.7		0.005	0.05	0.05	**4**
641.3		0.004	0.04	0.04	**4**
657.6	0.07	0.26			**1**
659.2	0.06	0.22			**1**
661.0	0.04	0.17			**1**
675.7			0.05	0.04	(GeOH)[b]
677.4			0.04	0.03	(GeOH)
679.1			0.04	0.03	(GeOH)
688.6		0.10	0.24	0.27	**6**
690.3		0.07	0.18	0.20	**6**
691.8		0.05	0.14	0.15	**6**
708.7	0.005	0.025			**1**
725.0		0.015	0.15	0.15	**4**
725.5		0.01	0.10	0.10	**4**
726.1		0.005	0.05	0.05	**4**
732.3			0.02	0.03	**5a**
734.5			0.02	0.03	**5a**
736.7			0.02	0.03	**5a**
738.1		0.025	0.05	0.05	?
747.0			0.09	0.10	**5a**
749.1		0.065	0.43	0.45	**5a**
751.3		0.055	0.35	0.36	**5a**
753.5		0.05	0.30	0.31	**5a**
771.5			0.025	0.025	?
833.9		0.01	0.015	0.02	?
844.8		0.01	0.015	0.02	?
867.7		0.01	0.02	0.02	**6**
871.7		0.015	0.02	0.02	**6**
877.2		0.05	0.10	0.11	**6**
885.2	0.015	0.06			**1**
897.8	0.08	0.20			**2**
924 br	0.02	0.04	0.04	0.04	**6**
926.0			0.035	0.035	**5a**
930 br	0.010	0.025	0.025	0.025	?
961.9	0.004	0.012	0.012	0.012	**3**
964.3	0.003	0.008	0.008	0.008	**3**
966.6	0.002	0.006	0.006	0.006	**3**
971.4		0.064	0.625	0.72	**5a**
972.6		0.06	0.60	0.68	**5a**
974.5		0.056	0.48	0.56	**5a** (masks **5b**)
1304.5			0.06	0.06	?
1544		0.02	0.05	0.06	O_2 complex
1586.1	0.04	0.12			**2**
1741.1	0.17	0.58			**1**
1757.5	0.015	0.06			**1**
1777.2	0.14	0.34			**2**
1794.4	0.09	0.21			**2**
1813.6	0.14	0.34			**2**
2076.6					**3**
2079.6					**3**
3597.4	0.12	0.31			**2**
3630.7		0.16	1.60	2.00	**5a**
3652.0	0.07	0.26			**1**
3686.9	0.23	0.70			**2**

[a] Photolysis A is 590–1000 nm, B is 380–1000 nm, C is 290–1000 nm, D is 220–1000 nm. [b] Tentative identification.

1490.1 cm^{-1} and a triplet at 1495.7, 1496.3, and 1497.0 cm^{-1} also belonging to species **3**. All these **3** absorptions came slightly to lower energy of the GeD_4 parent which came at 1513 and 1540 cm^{-1}. In the Ge=O stretching region a triplet due to species **5b** had components at 970.4, 972.8, and 975.2 cm^{-1}. The triplet (species **6**) which came in the Ge–O stretching region at 688.6, 690.2, and 691.8 cm^{-1} (in $GeH_4/^{16}O_3$ experiments) showed a blue shift with GeD_4, moving to 710.6, 711.8, and 713.0 cm^{-1}. In the low-frequency region, the species **1** band at 565.0 cm^{-1} and the species **5a** band at 396.9 cm^{-1} shifted to 420.3 and 295.4 cm^{-1}, respectively, on deuteriation (H/D ratios of 1.344). The deuterium shifts of other bands are given in Table II.

TABLE II: Isotopic Absorptions (cm^{-1}) Appearing on Photolysis of the Germane–Ozone Complex in Solid Argon

H, ^{16}O	H, ^{18}O	D, ^{16}O	D, ^{18}O	assignt
		209.5	200	**5a**
		243.6	230.7	**5a**
396.9	396.0	295.4	293.1	**5a**
421.5	419.8			?
466.0	463.9			?
566.0	563.0	420.3	417.4	**1**
		615.4	613.4	**3**
		616.4	614.6	**3**
		617.3	615.8	**3**
			617.0	**3**
638.2	609.9			**4**
639.7	611.6			**4**
641.3	613.3			**4**
657.6	629.3	642.0	621.0	**1**
659.2	631.0	643.6	622.8	**1**
661.0	632.8	645.4	624.6	**1**
675.7	644.7	673.5	644.8	(GeOH)
677.4	646.4	675.0	646.4	(GeOH)
679.1	648.2	676.4	648.1	(GeOH)
688.6	658.7	710.6	700.2	**6**
690.3	660.3	711.8	701.0	**6**
691.8	661.9	713.0	702.0	**6**
725.0		724.0		**4**
725.5	689.7	724.5		**4**
726.1		725.1		**4**
732.3	700.3	733.8		**5a**
734.5	702.4	735.3		**5a**
736.7	704.8	737.0		**5a**
738.1				
747.0				**5a**
749.1	716.9	748.4	714.3	**5a**
751.3	718.0	750.7	716.6	**5a**
753.5	721.0	752.8	719.0	**5a**
771.5	766.9			?
777.2		775.2		**4**
779.5		777.5		**4**
781.7		779.7		**4**
833.9				?
844.8				?
867.7	865.9	623.4	622.9	**6**
871.7	871.7	635 br	635 br	**6**
877.2	876.1			**6**
885.2	880.4	685.4	668.6	**1**
897.8	897.8	646.4	646.4	**2**
924 br	918 br			**6**
926.0	921.8			**5a**
961.9		967.7	923.3	**3**
964.3		965.3	920.6	**3**
966.6		963.2	918.1	**3**
971.4	915.3		929.2	**5a**
972.6	916.5	*a*	932.0	**5a**
974.5	917.7		934.7	**5a**
		1028.4	996.9	**5a**
1304.5	1297.2			?
1544	1457.4	*b*	1457.4	O_2 complex
1586.1	1580.1	1173.6	1164.8	**2**
1741.1	1738.3	1257.6	1257.1	**1**
1757.5	1750.1	1257.6	1257.1	**1**
1777.2	1777.2	1281.6	1281.6	**2**
1794.4	1794.4	1293.3	1293.3	**2**
1813.6	1813.6	1308.9	1308.9	**2**
2076.6	2076.5	1490.1	1489.9	**3**
2079.6	2079.5	1496.3	1496.2	**3**
3597.4	3590.3	2627.8	2617.2	**2**
3630.7	3619.5	2677.5	2661.7	**5a**
3652.0	3640.6	2695.1	2678.8	**1**
3686.9	3672.5	2738.5	2718.3	**2**

[a] Fermi resonance interaction gave rise to bands at 971.4, 972.2, 973.3, 973.9, 974.5, 975.8, and 977.0 cm^{-1}. [b] Masked by GeD_4 parent.

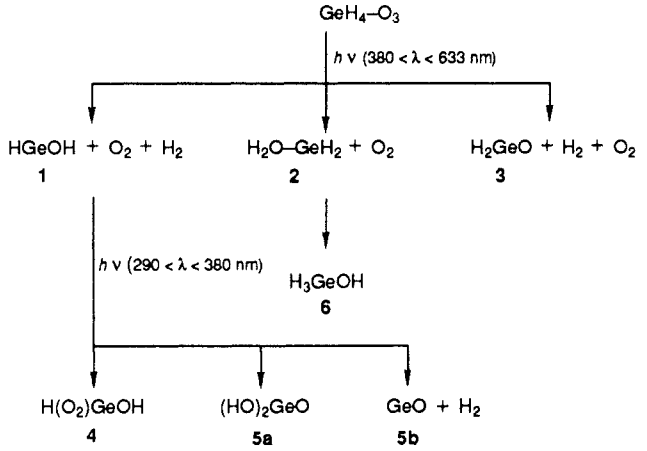
GeD_4 + $^{18}O_3$. Two triplets in the Ge=O stretching region belonging to species **5a** and **5b** are particularly noteworthy. The **5a** triplet appeared at 929.2, 932.0, and 934.7 cm^{-1} above its counterpart in $GeH_4/^{18}O_3$ experiments at 915.3, 917.8, and 920.0 cm^{-1}. The **5b** triplet appeared at 925.3, 927.9, and 930.5 cm^{-1},

TABLE III: Infrared Absorptions (cm^{-1}) for Isotopic Hydroxygermylene Species in Solid Argon

vibrational mode	HGeOH[a]	$HGe^{18}OH$	DGeOD	$DGe^{18}OD$
ν_1(O–H), A′	3652.0	3640.6	2695.1	2678.8
ν_2(H–Ge), A′	1741.1[b]	1738.3[c,d]	1257.6	1257.1
ν_3(GeOH), A′	885.2	880.4	685.4	668.6
ν_4(Ge–O), A′	657.5	629.3	642.0	621.0
	659.2	631.0	643.6	622.8
	661.0	632.8	645.4	624.6
ν_5(HGeO), A′	708.7	707.3	503.0	502.7
ν_6(torsion), A″	566.0	563.0	420.3	417.4

[a] Reference 5 gives 1741.3, 661.3, and 566.2 cm^{-1} for HGeOH. [b] In Fermi resonance with $2\nu_3$ which absorbs at 1757.6 cm^{-1}. [c] In Fermi resonance with $2\nu_3$ which absorbs at 1750.1 cm^{-1}. [d] ν(HGeOD) = 1744.3 cm^{-1}, $\nu(HGe^{18}OD)$ = 1744.3 cm^{-1}.

SCHEME I



the same as its counterpart in $GeH_4/^{18}O_3$ experiments.

$GeH_xD_{4-x}/^{16}O_3$. The Ge–H and Ge–D stretching regions were of particular interest in the mixed H/D germane experiment. In the Ge–H stretching region two bands appeared at 1782.5 and 1811.6 cm^{-1} along with the bands at 1777.2, 1794.4, and 1813.6 cm^{-1} which appeared in $GeH_4/^{16}O_3$ experiments (see Figure 2). Likewise, in the Ge–D stetching region two bands appeared at 1287.0 and 1307.4 cm^{-1} along with the bands at 1281.6, 1293.3, and 1308.9 cm^{-1} which appeared in $GeD_4/^{16}O_3$ experiments (see Figure 3).

Discussion

The products of matrix GeH_4/O_3 photolysis will be identified and reaction mechanisms will be presented in Scheme I.

Identification of the Photoproducts. Species **1** is identified as hydroxygermylene, HGeOH, in view of the close agreement with the matrix infrared spectrum reported by Kauffman et al.[5] (see Table III). This species, like hydroxysilylene,[1,12] is expected to be planar due to electron delocalization from oxygen into the vacant $4p_z$ atomic orbital of germanium. Unlike hydroxysilylene, which exhibits both cis and trans isomers,[1,12] there is evidence for only one isomer of hydroxygermylene. This is likely to be the cis planar isomer which has been calculated to be 1 kcal/mol more stable than the trans planar isomer.[2] Assignments of species **1** bands to cis planar HGeOH are given in Table III. The band at 3652.0 cm^{-1} which appears in the O–H stretching region and shifts 11.4 cm^{-1} with ^{18}O substitution is clearly the O–H stretch. The band at 1741.1 cm^{-1} which shows a large deuterium shift down to 1257.6 cm^{-1} is due to the Ge–H stretch, which is expected in this frequency region. The Ge–H stretching fundamental appears to be in Fermi resonance with the overtone of the Ge–O–H bending fundamental. This latter mode has a frequency of 885.2 cm^{-1}; thus its overtone should come slightly to the red of 1770.4 cm^{-1} (=2 × 885.2 cm^{-1}) on account of anharmonicity. For this reason, a weak band at 1757.6 cm^{-1} is most likely due to $2\nu_3$. In mixed GeH_xD_{4-x} (x = 0–4) experiments, a band at 1744.3 cm^{-1} is almost certainly due to the Ge–H stretch of HGeOD which no longer has this Fermi resonance interaction as the overtone of the Ge–O–D band does not appear in the Ge–H stretching region. The triplet with components at 657.6, 659.2, and 661.0 cm^{-1} is due to the Ge–O stretch; the three components are due to the three most abundant isotopes of naturally occurring germanium, namely ^{70}Ge, ^{72}Ge, and ^{74}Ge. The relative intensities of the components of this triplet are in accord with the natural abundances of ^{70}Ge, ^{72}Ge, and ^{74}Ge (20.5, 27.4, and 36.5%, respectively).[13] Two other germanium isotopes, ^{73}Ge and ^{76}Ge, are present in lesser abundances of 7.8% each as is evident from multiplets of species **5a** (see later). The band at 566.0 cm^{-1} is attributed to the torsion as it is the most intense of the bands due to deformational modes.

TABLE IV: Infrared Absorptions (cm^{-1}) for Isotopic GeH_2–H_2O Complexes in Solid Argon

GeH_2 Submolecule

mode	GeH_2	GeHD	GeD_2
		1811.6	
ν(Ge–H)	1813.6	1782.0	1308.9
	1777.2	1307.4	1281.6
		1287.0	
2δ(H–Ge–H)	1794.4		1293.3
δ(H–Ge–H)	897.8	*a*	646.4

H_2O Submolecule

	H_2O		HDO		D_2O	
mode	^{16}O	^{18}O	^{16}O	^{18}O	^{16}O	^{18}O
ν_s(O–H)	3597.4	3590.3	2682.3	2667.6	2627.8	2617.2
δ(H–O–H)	1586.1	1580.1	1398.4	1390.9	1173.6	1164.8
ν_{as}(O–H)	3686.0	3672.5	3637.3	3626.3	2738.5	2718.3

[a] Masked by GeH_xD_{4-x} absorptions.

Species **2** is identified as a germylene–water complex, GeH_2–H_2O, for reasons which are now outlined. Clearly the species **2** bands at 1586.1, 3597.4, and 3686.9 cm^{-1} are due to a complexed H_2O molecule as they appear close to the fundamentals of H_2O monomer in solid argon,[14] and their isotopic data is diagnostic. As can be seen from Figure 1, the two species **2** bands appearing in the O–H stretching region at 3597.4 and 3686.9 cm^{-1} have quite different ^{18}O shifts of 7.1 and 14.4 cm^{-1}, respectively, and this can be compared to an ^{18}O shift of 12.0 cm^{-1}, which is calculated for an isolated O–H diatomic in this region. These shifts are accounted for by the coupling of two equivalent O–H oscillators with a common oxygen atom. The doublets of species **2** bands in the O–H stretching region (as well as the H–O–H bending region) with the mixed $^{16,18}O$ reagent are indicative of one oxygen atom (see Figure 1). In addition, the bending fundamental of this H_2O submolecule gives way to a triplet with the partially deuteriated reagent, GeH_xD_{4-x}. Furthermore, two extra bands appear with GeH_xD_{4-x}, which are not present in pure GeH_4 or GeD_4 experiments, one coming in the O–H and the other coming in the O–D stretching regions (see Table IV). The foregoing isotopic data is indicative of two *equivalent* H atoms.

The triplet of species **2** bands at 1777.2, 1794.4, and 1813.6 cm^{-1} and one other band at 897.8 cm^{-1} belong to a GeH_2 submolecule. The band at 897.8 cm^{-1} with a large deuterium shift to 646.4 cm^{-1} is clearly appropriate for the H–Ge–H bending deformation, and it comes close to the frequency of 920 cm^{-1} reported[11] for isolated GeH_2. There is one more band than expected in the Ge–H stretching region. However, the frequency of 1794.4 cm^{-1} is very close to twice that of 897.8 cm^{-1} (2 × 897.8 = 1795.6 cm^{-1}) and for this reason the band at 1794.4 cm^{-1} is likely to be the overtone of the H–Ge–H bend, and its intensity is probably enhanced by Fermi resonance interaction with the Ge–H stretches. Likewise in the GeD_2 isotope there is also an

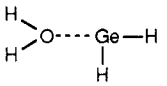
(12) Ismail, Z. K.; Hauge, R. H.; Fredin, L.; Kauffman, J. W.; Margrave, J. L. *J. Chem. Phys.* **1982**, *77*, 1617.

(13) *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986–7.

(14) Ayers, G. P.; Pullin, A. D. E. *Spectrochim. Acta* **1976**, *32A*, 1629.

extra band in the Ge–D stretching region at 1293.3 cm^{-1} which is the overtone of the D–Ge–D bend at 646.4 cm^{-1} (2 × 646.4 = 1292.8 cm^{-1}). To our knowledge the bond angle of isolated GeH_2 has not been measured, but as the two Ge–H stretching bands at 1777.2 and 1813.6 cm^{-1} have similar deuterium shifts (H/D ratios of 1.387 and 1.386, respectively) it appears that the bond angle of the present GeH_2 submolecule is close to 90°. This is in keeping with the 92° values predicted by ab initio calculations.[15] It can be seen from Figure 2 that the Ge–H stretches of species **2** come in the same region as species **1**, HGeOH, which are considerably lower than those of GeH_4 (2097 and 2134 cm^{-1} in solid argon). This seems to be characteristic of Ge–H bonds containing divalent Ge. Further examples are HGeCl (1862 cm^{-1})[16] and HGeBr (1858 cm^{-1})[17] which also have Ge–H stretching frequencies below GeH_4 values. This is presumably due to a weaker Ge–H bond with divalent Ge than with tetravalent Ge. Figure 2c–f shows the Ge–H stretching region in experiments with GeD_4 and mixed GeH_xD_{4-x} mixed isotopes. It is important to remember here that the GeD_4 sample contained 5% $GeHD_3$ impurity but no GeH_2D_2 was detected. As can be seen in Figure 2c which was obtained with GeD_4 and $^{16}O_3$ samples, there are two species **2** bands at 1782.0 and 1811.6 cm^{-1} in the Ge–H stretching region; it seems that these must arise from the $GeHD_3$ impurity in the GeD_4 sample. Such an isotopic pattern could arise if species **2** contained two *inequivalent* Ge–H oscillators. The same two species **2** bands are obtained in the experiment with GeD_4 and $^{18}O_3$ as can be seen in Figure 2d. The Ge–H stretching region in the experiment with GeH_xD_{4-x} and $^{16}O_3$ contains the triplet at 1777.2, 1794.4, and 1813.6 cm^{-1} obtained in $GeH_4/^{16}O_3$ experiments and the doublet at 1782.0 and 1811.6 cm^{-1} obtained in the "GeD_4"/$^{16}O_3$ experiment, but no additional species **2** bands (Figure 2e). An identical species **2** multiplet was obtained in the $GeH_xD_{4-x}/^{18}O_3$ experiment (Figure 2f). Figure 3 shows a similar isotopic pattern in the Ge–D stretching region. A strong triplet occurs at 1281.6, 1293.3, and 1308.9 cm^{-1} in $GeD_4/^{16}O_3$ and $GeD_4/^{18}O_3$ experiments (see Figure 3c,d). This triplet is present but weak in $GeH_xD_{4-x}/^{16}O_3$ and $GeH_xD_{4-x}/^{18}O_3$ experiments, but in both cases there are two additional features at 1287.0 and 1307.4 cm^{-1} (see Figure 3e,f). The triplet is due to GeD_2 and the two bands at 1287.0 and 1307.4 cm^{-1} are due to Ge–D stretches of GeHD.

The foregoing suggests that species **2** contains a GeH_2 submolecule with inequivalent Ge–H oscillators complexed to an H_2O moiety with equivalent O–H oscillators. A possible structure for the complex is the coplanar arrangement



2

Comparison of the Ge–H stretching frequencies of 1777.2 and 1813.6 cm^{-1} in species **2** with the values of 1864 and 1887 cm^{-1} reported for GeH_2 isolated in solid argon[11] suggests that both Ge–H bonds are weaker in this complex. The donation of electron density from the $3a_1$ orbital of water to GeH_2 in this complex is analogous to the bonding interaction described for adducts of metal atoms with water.[5]

Species **3** bands are attributed to the germanone molecule H_2GeO, which has not previously been observed. Unfortunately, the data on this species is somewhat fragmentary owing to low yield; nevertheless, germanium isotopic splittings, particularly in GeD_4 experiments, as well as comparison with theoretical studies have been very helpful. In normal isotopic experiments species **3** bands appeared at 961.9, 964.3, 966.6, 2076.6, and 2079.6 cm^{-1} with irradiation A and increased with irradiation B, but showed no change on irradiations C and D. The latter two bands are clearly Ge–H stretches, and the triplet at 961.9, 964.3, and 966.6 cm^{-1} is due to a Ge=O stretch as the germanium isotope splittings are quite diagnostic. An additional weak band at 803.8 cm^{-1} is tentatively assigned to the GeH_2 bending mode. Absorptions of germanone isotopes are collected in Table V along with vibrational frequencies from SCF calculations[2] (scaled by 0.89) for comparison. The calculated equilibrium geometry is a planar C_{2v} structure with GeO and GeH bond lengths of 1.634 and 1.547 Å, respectively, and an H–Ge–H bond angle of 112°.[2] The GeO bond length is slightly longer than the experimental bond length (1.62 Å) of diatomic GeO,[18] which is consistent with the GeO stretching frequency of H_2GeO coming approximately 8 cm^{-1} lower than that of diatomic GeO. Similarly, the GeH bond length of 1.547 Å is slightly longer than the experimental bond length of 1.53 Å of GeH_4,[19] consistent with the GeH stretching frequencies of H_2GeO coming slightly to the red of those of GeH_4. The different GeH bond lengths in GeH_4, H_2GeO, HGeOH, and GeH_2 can be accounted for in terms of sp^3 and sp^2 hybridization versus pure p bonds. The Ge–D stretches of $D_2Ge^{16}O$ at 1490.1 and 1495.7, 1496.3, and 1497.0 cm^{-1} also come slightly to the red of the Ge–D stretches of GeD_4. Furthermore, the germanium isotopic splitting on the latter triplet indicates that this is due to the antisymmetric D–Ge–D stretch. In order to reproduce the $^{70}Ge/^{72}Ge$ and $^{72}Ge/^{74}Ge$ isotopic shifts using the respective G matrix elements, a D–Ge–D valence bond angle of 100 ± 5° is required. This bond angle is slightly smaller than that obtained from the SCF calculations,[2] but it is the same as the experimentally determined F–Ge–F bond angle in F_2GeO.[6] The slightly larger H/D shift of the symmetric GeH_2 stretch (2076.6 → 1490.1 cm^{-1}) relative to the antisymmetric GeH_2 stretch (2079.6 → 1496 cm^{-1}) is consistent with an H–Ge–H angle of 100 ± 5°.

TABLE V: Infrared Absorptions (cm^{-1}) for Isotopic Germanone Species in Solid Argon

vibrational mode	calc[a]	$H_2Ge^{16}O$	$H_2Ge^{18}O$	$D_2Ge^{16}O$	$D_2Ge^{18}O$
ν_1(Ge–H str)	2009	2076.6	2076.5	1490.1	1489.9
ν_2(Ge=O str)	924	966.6		967.7	923.3
		964.3		965.3	920.6
		961.9		963.2	918.1
ν_3(H–Ge–H bend)	795	803.8	803.8	577[b]	577[a]
ν_4(Ge–H str)	1964	2079.6	2079.5	1497.0	1496.9
				1496.3	1496.2
				1495.7	1495.6
ν_5(H_2GeO rock)	558				617.0
ν_6(H_2GeO wag)	873			617.3	615.8
				616.4	614.6
				615.4	613.4

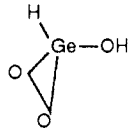
[a] Calculated and scaled, ref 2. [b] On shoulder of strong GeD_4 band at 595 cm^{-1}.

As can be seen from Table V, the SCF calculations predict a value of 873.1 cm^{-1} (after scaling) which is considerably higher than the value of 686.2 cm^{-1} (also after scaling) predicted for the out-of-plane wag of silanone, H_2SiO.[2] This is a reflection of the very high polarity of the Ge=O bond in germanone for which a dipole moment of 4.66 D has been calculated.[3] The result of this high polarity is a high force constant for the out-of-plane wag. Although this mode was not observed for H_2GeO, possibly because it was masked by other absorptions, a strong triplet at 615.4, 616.4, and 617.3 cm^{-1} on the shoulder of the $GeHD_3$ absorption centered on 625 cm^{-1} can be assigned to the wag of D_2GeO. The three components of this triplet are likely due to the $D_2{}^{72}Ge^{16}O$, $D_2{}^{74}Ge^{16}O$, and $D_2{}^{76}Ge^{16}O$ isotopes with a fourth band belonging to the $D_2{}^{70}Ge^{16}O$ isotope presumably obscured by the $GeHD_3$ band. In $GeD_4/^{18}O_3$ experiments a quartet is indeed observed at 613.4, 614.6, 615.8, and 617.0 cm^{-1} with an average $^{16}O/^{18}O$ red shift of 1.8 cm^{-1}. Taking the H_2GeO geometry as planar C_{2v} with GeO and GeH bond lengths of 1.63 and 1.55 Å, respectively, and a H–Ge–H bond angle of 100°, the $^{72}Ge/^{74}Ge$ and $^{74}Ge/^{76}Ge$

(15) Barthelat, J. C.; Roch, B. S.; Trinquier, G.; Satge, J. *J. Am. Chem. Soc.* **1980**, *102*, 4080.
(16) Isabel, R. J.; Guillory, W. A. *J. Chem. Phys.* **1971**, *55*, 1197.
(17) Isabel, R. J.; Guillory, W. A. *J. Chem. Phys.* **1972**, *57*, 1116.
(18) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
(19) Kattenberg, H. W.; Gabes, W.; Oskam, A. *J. Mol. Spectrosc.* **1972**, *44*, 425.

isotopic shifts of the wag of $D_2Ge^{16}O$ are calculated to be 1.0 and 0.9 cm^{-1}, respectively, in close agreement with the experimentally observed shifts, and the $^{16}O/^{18}O$ shift of the wag of D_2GeO is calculated as 2.6 cm^{-1} which is a little higher than the average $^{16}O/^{18}O$ shift of 1.8 cm^{-1}. Thus the above assignments are supported by observed and calculated isotopic shifts and SCF calculations.

Isotopic data for species **4** is also fragmentary, but it is tentatively identified as $H(O_2)GeOH$, the peroxo adduct of hydroxygermylene. The three bands observed for this species all come in the Ge–O stretching region and show germanium isotopic fine structure. However, the triplet at 725.0, 725.5, and 726.1 cm^{-1} shows $^{70}Ge/^{72}Ge$ and $^{72}Ge/^{74}Ge$ splittings of only 0.6 and 0.5 cm^{-1}, respectively, compared to 1.9 and 1.8 cm^{-1} which would be expected for a diatomic GeO oscillator in this region. Furthermore, this multiplet exhibits a very small deuterium shift of 1.0 cm^{-1} and a large ^{18}O shift down to 689.7 cm^{-1}. This data is consistent with an oxygen–oxygen stretching mode of species **4** shown below.



4

This mode has a degree of O–Ge–O deformation character which accounts for the germanium isotopic fine structure. The very weak multiplet at 777.2, 779.5, and 781.7 cm^{-1} shows $^{70}Ge/^{72}Ge$ and $^{72}Ge/^{74}Ge$ shifts of 2.2 and 2.3 cm^{-1} as well as a small deuterium shift of 2.0 cm^{-1}, which would be appropriate for a Ge–O symmetric stretch of species **4** with an O–Ge–O angle of less than 90°. The triplet at 638.2, 639.7, and 641.3 cm^{-1} shifting to 609.0, 611.6, and 613.3 cm^{-1} is very reasonable for a Ge–O stretch of the GeOH group. The lack of observation of a counterpart on deuteriation may be due to interaction with the Ge–O–D bend which is expected in this region. Finally, no species **4** multiplets were observed in scrambled $^{16,18}O_3$ experiments, suggesting a high isotopic dilution which would be expected for a species containing three O atoms.

Species **5a** is identified as germanic acid, $(HO)_2Ge{=}O$, for reasons which are now given. The spectrum of $(HO)_2Ge{=}O$ is consistent with that of a planar C_{2v} species similar to that of silicic acid, $(HO)_2SiO$, the silicon-containing analogue. Such a planar C_{2v} molecule has nine in-plane ($5A_1$ and $4B_1$) and three out-of-plane ($2B_2$ and $1A_2$) vibrations.

The strong triplet in the Ge=O stretching region at 971.4, 972.6, and 974.5 cm^{-1} is assigned to a mixture of the Ge=O stretching and symmetric Ge–O–H bending fundamentals which are both of A_1 symmetry. Clearly the $^{70}Ge/^{72}Ge$ and $^{72}Ge/^{74}Ge$ isotopic shifts of 1.2 and 1.9 cm^{-1} are too small for a pure Ge=O stretch as the GeO diatomic exhibits $^{70}Ge/^{72}Ge$ and $^{72}Ge/^{74}Ge$ shifts of 2.4 cm^{-1}. Furthermore, on ^{18}O substitution the triplet gives way to a very strong band at 963.9 cm^{-1} and a quintet with components at 912.8, 915.3, 916.5, 917.7, and 920.0 cm^{-1} (see Figure 4b). The strong 963.9-cm^{-1} band is presumably due to the symmetric $Ge{-}^{18}O{-}H$ bend and the quintet is due to the $Ge{=}^{18}O$ stretching mode for the five germanium isotopes ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge. The $^{70}Ge/^{72}Ge$, $^{72}Ge/^{74}Ge$, and $^{74}Ge/^{76}Ge$ isotopic shifts of 2.5, 2.4, and 2.3 cm^{-1} are reasonable for this mode.

The **5a** band at 926.0 cm^{-1} shifting to 921.8 cm^{-1} with ^{18}O is assigned to the antisymmetric Ge–O–H bend. In $GeH_xD_{4-x}/^{18}O_3$ experiments a band at 945.3 cm^{-1} is probably due to the Ge–O–H bend of $(H^{18}O)(D^{18}O)Ge{=}^{18}O$ as it is approximately intermediate between the Ge–O–H symmetric and antisymmetric bends of $(H^{18}O)_2Ge{=}^{18}O$ at 963.9 and 921.8 cm^{-1}, respectively.

The intense quartet at 747.0, 749.1, 751.3, and 753.5 cm^{-1} is assigned to the antisymmetric Ge–O stretch as it is near the antisymmetric Ge–F stretch of F_2GeO (746.7 cm^{-1})[6] and has similar germanium isotopic shifts (Figure 5). Likewise, the weak triplet at 732.3, 734.5, and 736.7 cm^{-1} can be assigned to the

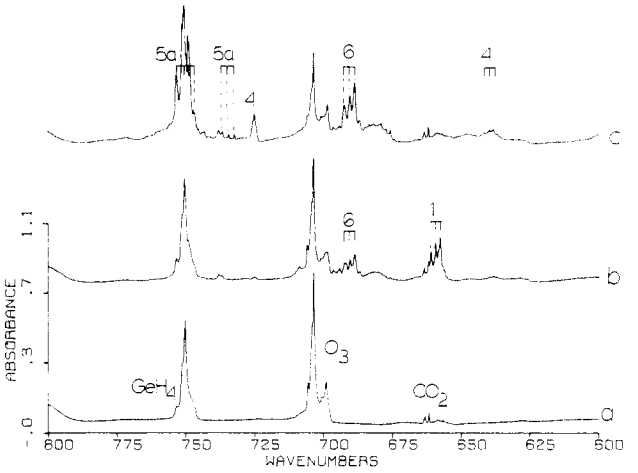


Figure 5. Infrared spectra in the 600–800-cm^{-1} Ge–O stretching region of a $Ar/GeH_4/^{16}O_3$ = 1200/3/4 sample (a) immediately after deposition, (b) after irradiation B, and (c) after irradiation D.

symmetric Ge–O stretch of species **5a** as it has reasonable germanium isotope shifts, and it comes in the same region as the symmetric Ge–F stretch of F_2GeO at 731.7 cm^{-1}. The **5a** bands at 739.9, 740.7, 741.6, 742.3, 743.7, and 744.3 cm^{-1} in $^{16,18}O_3$ experiments lie between the symmetric and antisymmetric Ge–O stretches of $(H^{16}O)_2Ge^{16}O$ and are likely due to the $Ge{-}^{16}O$ stretch in $(HO)_2GeO$ isotopes containing ^{16}O and ^{18}O atoms. In $GeH_4/^{18}O_3$ experiments, species **5a** triplets at 716.9, 718.9, and 721.0 cm^{-1} and at 700.3, 702.4, and 704.8 cm^{-1} can be assigned to the antisymmetric and symmetric $Ge{-}^{18}O$ stretches. Additionally, an intermediate triplet at 709.1, 711.4, and 713.8 cm^{-1} can be assigned to the $Ge{-}^{18}O$ stretch of $(H^{18}O)(H^{16}O)Ge{=}^{18}O$ which is present due to a small amount of ^{16}O impurity in the ^{18}O-enriched ozone.

The intense band at 396.9 cm^{-1} can be confidently assigned to the torsion of B_2 symmetry which is expected to give rise to a strong band. The torsion of A_2 symmetry is not expected to be observed as it is infrared forbidden in this C_{2v} molecule. The band in the O–H stretching region at 3630.7 cm^{-1} is clearly due to an O–H stretch of $(HO)_2GeO$. Two O–H stretches are expected for this species, one of A_1 and one of B_1 symmetry. However, there may be very little coupling of these two high-frequency O–H oscillators through the skeletal Ge–O modes, and in this case the two O–H stretches would be accidentally degenerate, which would explain the observation of only one O–H stretch.

In the low-frequency region a band at 243.5 cm^{-1} in $GeD_4/^{16}O_3$ experiments has an ^{18}O shift of 12.9 cm^{-1} which is appropriate for the symmetric O–Ge–O bending mode of $(DO)_2GeO$. This assignment is supported by the observation that the combination band of the symmetric Ge–O stretching and O–Ge–O bending modes of $D_2Ge^{16}O$ is in Fermi resonance with the Ge=O stretch in the 970-cm^{-1} region (see Table VI). A band at 209.5 cm^{-1} in $GeD_4/^{16}O_3$ experiments can be assigned to the O_2GeO wag of $(DO)_2GeO$ as it has an appropriate ^{18}O shift for this mode, and it appears at the same frequency as that reported for the analogous F_2GeO molecule.[6] The only fundamental which remains to be discussed is the O_2GeO rock. Unfortunately this mode was not observed, presumably due to low intensity, but it is expected in the 200-cm^{-1} region by analogy with F_2GeO.

Finally, for species **5a**, a strong band at 1028.4 cm^{-1} in $GeD_4/^{16}O_3$ experiments which shifts 31.5 cm^{-1} to 996.9 cm^{-1} in $GeD_4/^{18}O_3$ experiments is assigned to a combination band of O–H torsion and Ge–O symmetric stretch. The O–H torsion of B_2 symmetry and the Ge–O symmetric stretch of $(D^{16}O)_2Ge^{16}O$ come at 295.4 and 735.3 cm^{-1} with addition of these two giving a value of 1030.7 cm^{-1}. This comes a little higher than the observed combination band at 1028.4 cm^{-1} probably on account of anharmonicity.

Species **5b** is identified as the isolated GeO diatomic by comparison with earlier matrix infrared studies of this species.[4,5] As can be seen from Table VII, there is very good agreement with

TABLE VI: Infrared Absorptions (cm^{-1}) for Isotopic $(HO)_2GeO$ Species in Solid Argon

mode	H, ^{16}O	H, ^{18}O	D, ^{16}O	D, ^{18}O
ν(O–H), A_1 or B_1	3630.7	3619.5	2677.5	2661.7
		920.0	975.8	
ν(Ge=O), A_1	974.5	917.7	974.5	934.7
	972.6	916.5	973.9	932.0
	971.4	915.3	972.2	929.2
		912.8	971.4	
δ_s(Ge–O–H), A_1	955.1	963.9		726.8
δ_{as}(Ge–O–H), B_1	926.0	921.8		
ν_{as}(Ge–O), B_1	753.5	721.0	752.8	719.0
	751.3	718.9	750.7	716.6
	749.1	716.9	748.4	714.3
	747.0			
ν_s(Ge–O), A_1	736.7	704.8	737.0	
	734.5	702.4	735.3	
	732.3	700.3	733.8	
τ(O–H), B_2	396.9	396.0	295.4	293.1
δ_s(O–Ge–O), A_1			243.6	230.7
$\omega(O_2GeO)$, B_2			209.5	200
τ(O–H) + ν_s(Ge–O)			1028.4	996.9

TABLE VII: Infrared Absorptions (cm^{-1}) for Isotopic GeO Species in Solid Argon

	^{70}Ge	^{72}Ge	^{73}Ge	^{74}Ge	^{76}Ge	ref
^{16}O	980.2	977.7	976.9	975.3	973.1	*a*
^{16}O	975.3	972.9		970.8		*b*
^{16}O	975.2	972.8		970.4		*c*
^{18}O	934.0	931.0		928.5		*a*
^{18}O	930.5	927.9		925.3		*c*

[a] Reference 4. [b] Reference 5. [c] This work.

these previous studies in support of this identification. It is of interest that the observed $^{70}Ge/^{72}Ge$ and $^{72}Ge/^{74}Ge$ shifts of 2.6 cm^{-1} in $Ge^{18}O$ are slightly greater than the $^{70}Ge/^{72}Ge$ and $^{72}Ge/^{74}Ge$ shifts of 2.4 cm^{-1} in $Ge^{16}O$ as the Ge atom oscillates against the slightly heavier ^{18}O atom.

Species **6** is identified as germanol, H_3GeOH, based on isotopic shifts and a comparison of its matrix infrared spectrum with the gas-phase infrared spectrum of the analogous H_3GeF molecule.[20] In fact it is remarkable how alike the Ge–F and Ge–O bonds are (a similar resemblance is exhibited by Si–F and Si–O linkages),[12] as has already been seen in the comparison of species **5a**, $(HO)_2GeO$, with F_2GeO. The triplet at 688.6, 690.2, and 691.8 cm^{-1}, which shifts 29.9 cm^{-1} with ^{18}O and gives way to a doublet of triplets with scrambled $^{16,18}O_3$, is due to the Ge–O stretch. This mode appears within a few wavenumbers of the Ge–F stretch of H_3GeF (689 cm^{-1}).[20] On deuteriation the Ge–O stretch is blue-shifted to 710.6, 711.8, and 713.0 cm^{-1} presumably due to interaction with Ge–O–D and GeD_3 deformation modes of the same symmetry. There is likely to be considerable interaction with the Ge–O–D bend, in particular, as the Ge–O stretch of H_3GeOH is blue-shifted by approximately 21 cm^{-1} whereas the Ge–F stretch of H_3GeF is blue-shifted by only 7 cm^{-1}.[20] A broad band at 924 cm^{-1} is assigned to the Ge–O–H bend. Unfortunately its deuterium counterpart is not observed, but it very likely comes in the region of the Ge–O stretch. A band at 871.7 cm^{-1} showing no ^{18}O shift is suitable for the GeH_3 deformation of A″ symmetry, and it also comes very close to the same mode in H_3GeF which has been reported at 874 cm^{-1}.[20] Bands observed for H_3GeOH and their assignments are given in Table VIII. No Ge–H stretches were observed because they are likely to come in the 2100–2140-cm^{-1} region, where these modes are observed in germyl halides,[20] and this region is masked by GeH_4 parent bands.

Finally the triplet at 675.7, 677.4, and 679.1 cm^{-1} which shifts to 644.7, 646.4, and 648.2 cm^{-1} with ^{18}O and shows a small deuterium shift to 673.5, 675.0, and 676.4 cm^{-1} is tentatively assigned to GeOH. The ^{18}O shift of 31.0 cm^{-1} of this triplet and the fact that it gives rise to a doublet of germanium triplets with scrambled $^{16,18}O_3$ is evidence for the Ge–O bond. Furthermore, the small but increasing deuterium red shifts of 2.2, 2.4, and 2.7 cm^{-1} of the triplet components at 675.7, 677.4, and 679.1 cm^{-1}, respectively, suggest that there is a mode just above the $Ge-^{16}O$ stretch when this species is deuteriated, as would be expected for the $Ge-^{16}O-D$ bend. This is consistent with the fact that no deuterium shift is observed for the $Ge-^{18}O$ stretch at 644.7, 646.4, and 648.2 cm^{-1} which presumably does not come as close in energy to the Ge–O–D bend. H_2GeOH would also contain the GeOH grouping, but it is very unlikely that the 675.7-, 677.4-, and 679.1-cm^{-1} triplet is due to this radical species as there appeared to be no evidence that it contains Ge–H linkages. In particular, bands due to Ge–H stretches would be expected in the 1800-cm^{-1} region by analogy with H_2GeCl,[16] and H_2GeBr,[17] but none were observed which exhibited the same behavior as the 675.7-, 677.4-, and 679.1-cm^{-1} triplet.

TABLE VIII: Infrared Absorptions (cm^{-1}) for Germanol Isotopes in Solid Argon

mode	H, ^{16}O	H, ^{18}O	D, ^{16}O	D, ^{18}O
δ(Ge–O–H), A′	924 br	918 br		
$\delta(GeH_3)$, A″	871.7	871.7	635 br	635 br
$\delta(GeH_3)$, A′	877.2	876.1		
$\delta(GeH_3)$, A′	867.6	865.9	623.4	622.9
	691.8	661.9	713.0	702.0
ν(Ge–O), A′	690.2	660.3	711.8	701.0
	688.6	658.7	710.6	700.2

Conclusions

Germanone, $H_2Ge{=}O$, the germylene–water complex, $H_2O–GeH_2$, and hydroxygermylene, HGeOH, were formed on red mercury arc photolysis of a $GeH_4–O_3$ complex, and increased with more energetic irradiation ($1000 > \lambda > 380$ nm)(Scheme I). On still more energetic radiation ($1000 > \lambda > 290$ nm) hydroxygermylene disappeared to form germanic acid, $(HO)_2GeO$, its peroxo isomer, $H(O_2)GeOH$, and GeO. The $H_2O–GeH_2$ complex gave way to germanol, H_3GeOH, presumably via insertion of germylene into an O–H bond of water. Germanone was unaffected by this more energetic irradiation. These new species were identified by ^{18}O and deuterium isotopic substitution as well as isotopic fine structure of naturally occurring germanium, and by mechanistic considerations.

Apparently, the $GeH_4–O_3$ complex exhibits a stronger submolecule interaction, particularly in the red excited state of ozone, than does the $SiH_4–O_3$ complex, which required ultraviolet photolysis for reaction.

There is very little inductive effect on the Ge=O stretching frequency due to electronegative substituents, which is in stark contrast to a much greater effect on the Si=O stretching frequency. For example, the $^{74}Ge{=}O$ stretching frequencies of F_2GeO,[6] $(HO)_2GeO$, GeO, and H_2GeO come at 989.9, 971.4, 970.4, and 961.9 cm^{-1}, respectively, in solid argon whereas the Si=O stretching frequencies of F_2SiO,[21] $(HO)_2SiO$, SiO, and H_2SiO[1] come at 1309, 1270, 1226, and 1202 cm^{-1}. This can be related to the extremely high polarity of the Ge=O bond which has been calculated as 4.66 D in germanone.[3] It is likely that there is only a small degree of electron withdrawal by electronegative substituents bonded to the polar Ge=O functionality. As has previously been noted, this high polarity is expected to enhance the reactivity of species containing Ge–O double bonds with respect to cycloaddition or polymerization reactions.[3]

Finally, the Ge–H stretching frequencies decrease in the order $GeH_4 > H_2GeO > GeH_2$ presumably due to increasing germanium p orbital character along this series.

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