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Matrix Reactions of Methylsilanes and Oxygen Atoms

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The reactions of oxygen atoms and substituted methylsilanes have been investigated in argon matrices at 14-17 K. Products were identified by using isotopic $^{18}O_3$ precursor and deuterium substitution in the Si-H bonds. With $MeSiH_3$, Me_2SiH_2, and Si_2H_6, the silanols $MeSiH_2OH$, Me_2SiHOH, and SiH_3SiH_2OH were formed, respectively. These molecules contain the Si-O-H functional group with 3708-3711-cm^{-1} O-H stretching frequencies. For Me_4Si, the carbinol Me_3SiCH_2OH was produced with a lower 3637-cm^{-1} O-H stretching frequency. Me_3SiH was different: the silanol was not observed, but instead a product tentatively identified as $CH_2{=}Si(OH)Me$ was formed. Also, the silanones H_2SiO and Me(H)SiO were produced from $MeSiH_3$, Me(H)SiO and Me_2SiO were formed with Me_2SiH_2, and Me_2SiO was again observed with Me_3SiH. These silanones contain the Si═O functional group with stretching frequencies of 1201-1209 cm^{-1}.

Introduction

A previous study of matrix reactions of SiH_4 and oxygen atoms provided a unique method of synthesis for molecules containing SiOH and Si═O functional groups.[1] The limited vibrational data on these species, which include Cl_3SiOH[2] and $Me_2Si(OH)_2$[3] and a detection of $Me_2Si{=}O$,[4] justify a thorough parallel study of the reactions of methyl-substituted silanes and oxygen atoms. Infrared spectroscopic evidence for methyl- and dimethylsilanones, formed in the reactions of methyl-substituted silanes and oxygen atoms, was reported briefly in a recent communication.[5]

Experimental Section

Apparatus. The cryogenic refrigeration system and vacuum vessel have been described previously.[6] All spectra were recorded on a Perkin-Elmer 983 spectrophotometer over the range 180-4000 cm^{-1}; the frequency accuracy of band locations is ±0.2 cm^{-1}. Samples were irradiated for periods up to 1.0 h by using a BH-6 high-pressure mercury arc lamp (1000 W; Illumination Industries Inc.) in combination with Corning glass and a 10-cm water filter, which exposed the samples to the following wavelength ranges: A, 420-1000 nm; B, 290-1000 nm; C, full arc 220-1000 nm.

Chemicals. Ozone was generated by Tesla coil discharge of oxygen (normal isotopic, Burdett, USP grade; 55% and 95% ^{18}O enriched, Yeda) in a Pyrex tube immersed in liquid N_2: residual O_2 was removed by pumping by 77 K.[7] $MeSiH_3$, Me_2SiH_2, Me_3SiH, and Me_4Si were obtained from Petrarch Systems. Si_2H_6 was prepared by reduction of Si_2Cl_6 (Pfaltz and Bauer) with $LiAlH_4$ (Aldrich) in ether solution.[8] Deuteriated silanes were prepared by reduction of the chlorides (Aldrich) with $LiAlD_4$ (Aldrich) in ether solution.[8]

Procedure. (i) Samples of methyl-substituted silane ($Ar/Me_nSiH_{4-n} = 200/1$, $n = 1, 2, 3, 4$) or disilane and ozone ($Ar/O_3 = 150/1$) were codeposited at 14-17 K through two separate spray-on lines at equal rates of 1-2 mmol/h for 10 h. Samples were irradiated after deposition, and more spectra were recorded.

(ii) O atoms were generated by the microwave discharge (Burdick; 2450 MHz) of an Ar/O_2 stream in a 6-mm-o.d. quartz tube directed at the cold window using Ar/O_2 gas mixtures of 100/1. The argon/O_2/O atom stream was codeposited with Ar/methylsilane samples of approximately 10 h.

Results

$MeSiH_3$ + $^{16}O_3$. An infrared spectrum recorded immediately after reagent codeposition is shown in Figure 1a. The infrared spectrum of $MeSiH_3$ isolated in an argon matrix is in agreement with a previous study[9] except for the 1400-cm^{-1} region. The $MeSiH_3$ molecule almost certainly assumes a C_{3v} conformation as in the gas phase.[10] In the 1350-1459-cm^{-1} region, where the ν_9(e) CH_3 deformation is expected by comparison with gas-phase studies,[10-12] a strong band was observed at 1440.5 cm^{-1} and a doublet of medium intensity at 1376.5 and 1381.2 cm^{-1} with weaker site splittings at 1389.5 and 1395.7 cm^{-1}. The split bands are most likely due to Fermi resonance between ν_9 and the $\nu_{11} + \nu_{12}$ mode as has been noted before[9] with the band at 1440.5 cm^{-1} belonging to ν_9 and the doublet at 1376.5 and 1381.2 cm^{-1} belonging to $\nu_{11} + \nu_{12}$. For $MeSiD_3$, $\nu_{11} + \nu_{12}$ was red-shifted to the 1200-1300-cm^{-1} region and a single, strong band was observed at 1421.8 cm^{-1}. In gas-phase studies of $MeSiH_3$, ν_9 has been assigned the frequencies 1403 cm^{-1} [10,11] and 1430 cm^{-1},[12] and this discrepancy is almost certainly due to complications in the spectrum arising from the Fermi resonance interaction.

TABLE I: Absorbances of Product Bands after Irradiations A, B, and C of Argon Matrix Containing $MeSiH_3$ and $^{16}O_3$

ν/cm^{-1}	A	B	C	ident[a]
509.7	0.01	0.02	0.04	MS
593.0			0.03	
718.5	0.11	0.24	0.58	MS
734.4	0.03	0.06	0.19	
752.4	0.025	0.05	0.15	
797.4	0.04	0.075	0.20	MS
835.3	0.02	0.05	0.18	
877.1	*b*	*b*	*b*	
922.4	*b*	*b*	*b*	
962	*b*	*b*	*b*	
976.7	0.05	0.13	0.45	MS
1017.4		0.03	0.11	
1201.7		0.01	0.04	B
1207.6		0.03	0.11	M
1303.3			0.03	CH_4
2127.4	0.12	0.24	0.62	MS
2138.0	0.12	0.26	0.64	MS
3716.0	0.045	0.105	0.30	MS

[a] MS denotes methylsilanol, M identifies methylsilanone, and B denotes silanone. [b] Unresolved in survey scan from $MeSiH_3$ precursor.

Irradiation A produced new bands which are listed in Table I. These bands increased with irradiations B and C (Table I). Figure 1b shows the 180-4000-cm^{-1} region of the survey infrared spectrum which was recorded following irradiation C. Particularly diagnostic absorptions include a band in the O-H stretching region at 3716.0 cm^{-1} (Figure 2a), two strong bands in the Si-H stretching region at 2127.4 and 2138.0 cm^{-1} (Figure 2b), and a

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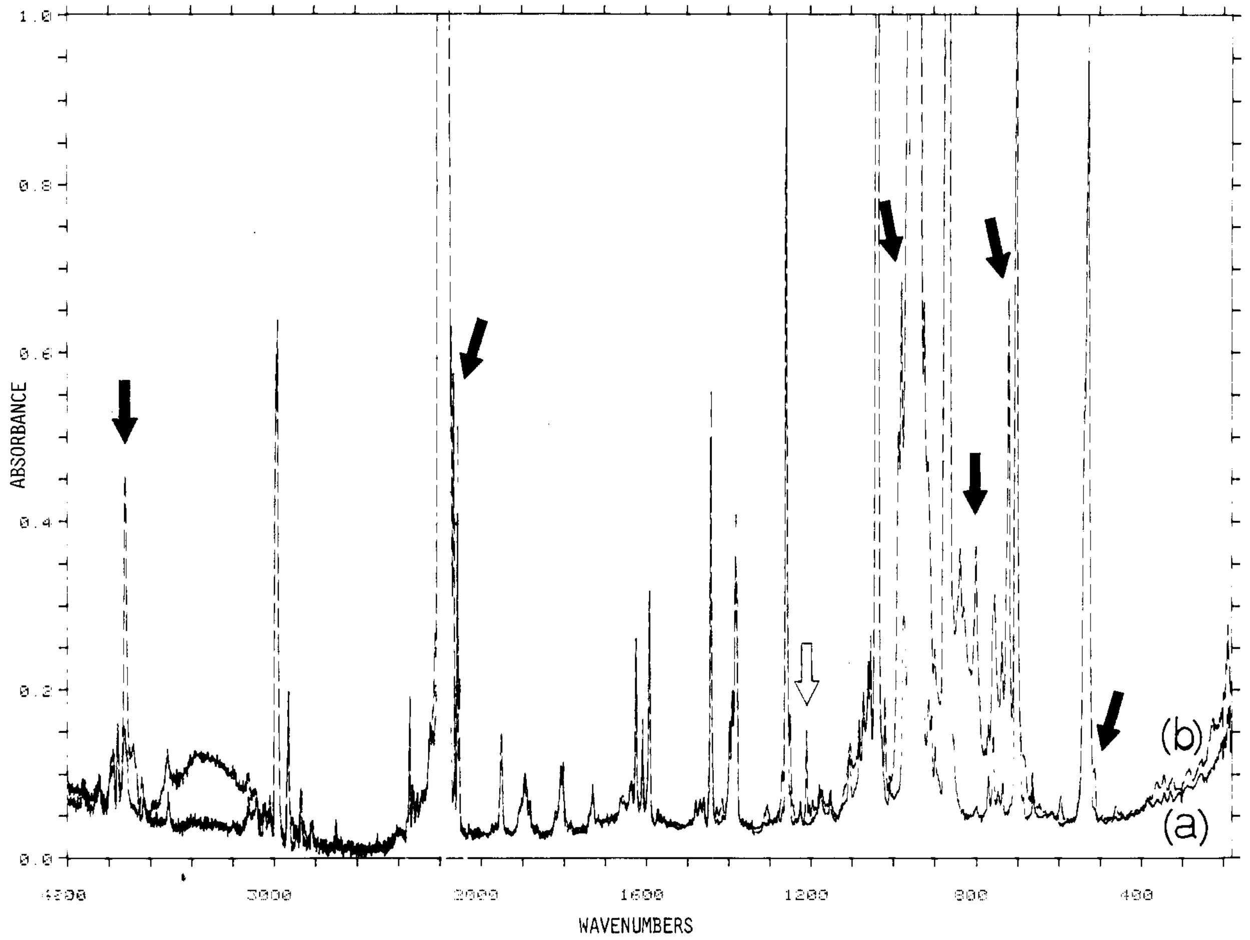

Figure 1. Infrared spectra of a sample of Ar/MeSiH$_3$/^{16}O$_3$ = 1200/3/4 in the 180–4000-cm^{-1} region (a) immediately after deposition at 14–17 K; (b) after irradiation C. Bold arrows indicate methylsilanol (MS) absorptions, and the light arrow shows a methylsilanone (M) band.

TABLE II: Isotopic Absorptions (cm^{-1}) Appearing on Irradiation of Argon Matrix Containing Methylsilane and Ozone

CH$_3$SiH$_3$		CH$_3$SiD$_3$		
^{16}O$_3$	^{18}O$_3$	^{16}O$_3$	^{18}O$_3$	ident
509.7	509.8			MS
593.0	590.1			
718.5	717.8	548 br	547 br	MS
734.4	732.8			
752.4	751.4			
797.4	793.5	786.0	783.4	MS
877.1	877.1			
		876.4 vs	859.4	MS
910	913.0			
922.4	922.2			
962	962.6			
976.7	*a*	753.7	745.4	MS
1017.4	*a*			
1201.7	1162.7			B
1207.6	1170.6	1202.3	1165.4	M
1303.3	1303.3	1303.3	1303.3	CH$_4$
2127.4	2127.4	*b*	*b*	MS
2138.0	2138.0	*b*	*b*	MS
3716.0	3704.2	2739.9	2720.9	MS

[a] Masked by ν_3 of ^{18}O$_3$. [b] Unresolved from MeSiD$_3$ precursor.

strong band at 718.5 cm^{-1} (Figure 2c). Bands in the Si=O stretching region at 1207.6 cm^{-1} and 1201.7 cm^{-1} (labeled M and B, respectively, in Figure 2d) were not present following irradiation A but appeared on irradiation B and increased markedly on irradiation C.

MeSiH$_3$ + ^{18}O$_3$. Similar experiments were performed with MeSiH$_3$ and ^{18}O$_3$ (95% ^{18}O). In the O–H stretching region, the MS band at 3716.0 was red-shifted to 3704.2 cm^{-1} and the M band at 1207.6 cm^{-1} was red-shifted to 1170.6 cm^{-1}. The other bands showed little or no ^{18}O shift as can be seen from Table II.

TABLE III: Isotopic Absorptions (cm^{-1}) Appearing on Full-Arc Irradiation of Argon Matrix Containing Disilane and Ozone

Si$_2$H$_6$		Si$_2$D$_6$	
^{16}O$_3$	^{18}O$_3$	^{16}O$_3$	^{18}O$_3$
521.7	521.0		
748 br	746 br	556.9	555.4
855.0	852.1	637.4	635.9
		862.0	836.0
950.6	948.4		
961.6	961.6	704.4	704.4
3708.5	3697.0	2733.5	2716.8

An experiment with ^{16,18}O$_3$ (55% ^{18}O) gave only the photoproducts from the pure ^{16}O$_3$ and ^{18}O$_3$ isotopic experiments.

MeSiD$_3$ + O$_3$. Samples of MeSiD$_3$ and ozone were codeposited and photolyzed; new bands are listed in Table II. A very intense MS absorption at 876.4 cm^{-1} was red-shifted to 859.4 cm^{-1} with ^{18}O. This ^{18}O shift of 17.0 cm^{-1} is considerably higher than the ^{18}O shift of any of the MS bands in this spectral region in CH$_3$SiH$_3$ experiments. Another noteworthy MS band appeared at 2739.9 cm^{-1}, in the O–D stretching region, and showed a red shift of 19.0 cm^{-1} with ^{18}O. The M band at 1207.6 cm^{-1} shifted to 1202.3 cm^{-1} with MeSiD$_3$.

MeSiH$_3$ + O. Samples of methylsilane (Ar/MeSiH$_3$ = 100/1) were codeposited with oxygen (Ar/O$_2$ = 100/1) passed through a microwave discharge tube for 8 h. Absorptions observed in MeSiH$_3$/O$_3$ experiments that belong to species MS (Table I) also appeared here. Other bands not present in MeSiH$_3$/O$_3$ experiments were produced here and with vacuum-ultraviolet photolysis of Ar/MeSiH$_3$ matrices alone.[13] With ^{18}O, isotopic MS bands were also observed.

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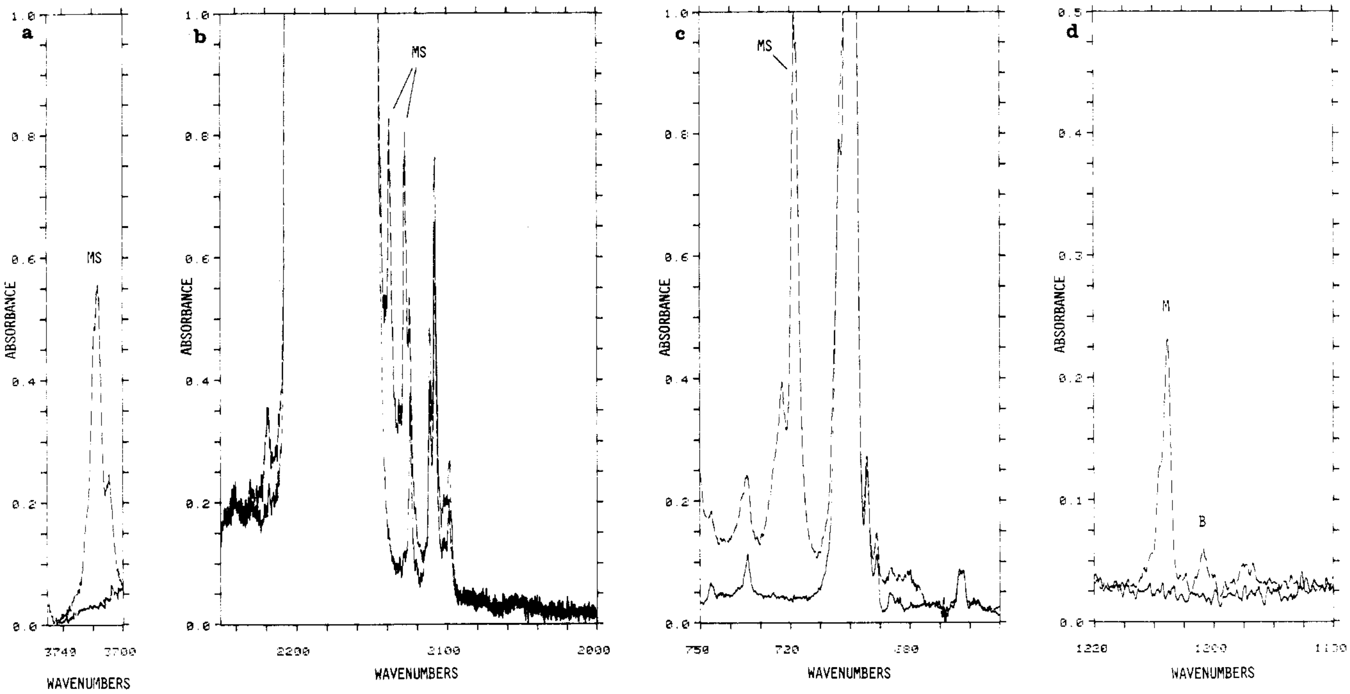

Figure 2. (a) Infrared spectrum of a sample of Ar/MeSiH$_3$/$^{16}O_3$ = 1200/3/4 before (solid trace) and after (dashed trace) irradiation C at 14–17 K in the 2000–2250-cm^{-1} region. (b) Infrared spectrum of a sample of Ar/MeSiH$_3$/$^{16}O_3$ = 1200/3/4 before (solid trace) and after (dashed trace) irradiation C at 14–17 K in the 2000–2250-cm^{-1} region. (c) Infrared spectra of a sample of Ar/MeSiH$_3$/$^{16}O_3$ = 1200/3/4 before (solid trace) and after (dashed trace) irradiation C at 14–17 K in the 650–750-cm^{-1} region. (d) Infrared spectra of a sample of Ar/MeSiH$_3$/$^{16}O_3$ = 400/1/1 before (solid trace) and after (dashed trace) irradiation C at 12 K in the 1160–1220-cm^{-1} region.

TABLE IV: Absorptions of Product Bands after Irradiations A, B, and C of Argon Matrix Containing Me_2SiH_2 and $^{16}O_3$

ν/cm^{-1}	A	B	C	ident[a]
283	0.01	0.03	0.05	DS
616.2	0.02	0.05	0.09	DS
707.3	*b*	*b*	*b*	DS
711.0	*b*	*b*	*b*	DS
738.5	0.01	0.05	0.08	
757.2	0.05	0.24	0.38	DS
764.5	0.04	0.20	0.28	DS
808.8	0.13	0.16	0.31	
819.4	0.27	0.50	1.25	DS
925	*b*	*b*	*b*	DS
1207.4		0.01	0.04	M
1209.6	0.015	0.035	0.095	D
1303.3			0.04	CH_4
2111.0	0.25	0.55	1.25	DS
3717.1	0.05	0.20	0.29	DS

[a] DS denotes dimethylsilanol, M identifies methylsilanone, and D denotes dimethylsilanone. [b] Unresolved in survey scan from Me_2SiH_2 precursor.

Si_2H_6 + O_3. The infrared spectrum of Si_2H_6 in solid argon was in good agreement with the previously reported spectrum.[14] Exposure of Ar/Si_2H_6/O_3 matrices to full-arc radiation produced new bands which are listed in Table III. Particularly diagnostic absorptions appeared at 3708.5 and 748 cm^{-1}. No product bands were observed in the Si—O and Si═O stretching regions. A similar experiment with Si_2H_6 and $^{18}O_3$ shifted the O–H stretching band to 3697.0 cm^{-1} as given in Table III. An experiment with Si_2H_6 and scrambled $^{16,18}O_3$ (55% ^{18}O) gave only bands which were produced in $^{16}O_3$ and $^{18}O_3$ experiments.

Si_2D_6 + O_3. The diagnostic absorption appeared in the O–D stretching region at 2733.5 cm^{-1} following photolysis of Si_2D_6 and ozone and was red-shifted to 2716.8 cm^{-1} with $^{18}O_3$. A strong product band at 862.0 cm^{-1} was shifted to 836.0 cm^{-1} with ^{18}O substitution.

Me_2SiH_2 + $^{16}O_3$. An infrared spectrum recorded immediately after reagent codeposition is shown in Figure 3a. The spectrum of Me_2SiH_2 in solid argon is in good agreement with gas-phase data.[15] Exposure of Ar/Me_2SiH_2/$^{16}O_3$ matrices to irradiation with the 590-nm cutoff filter produced new DS bands which are listed in Table IV along with their intensities. These bands increased intensity with irradiations A–C (Table IV). Figure 3b shows the 180–4000-cm^{-1} region of the survey infrared spectrum which was recorded following irradiation C. Particuarly diagnostic DS bands come at 3717.1 cm^{-1} in the O–H stretching region (Figure 4a), 2111.0 cm^{-1} in the Si–H stretching region (Figure 4b), at 707.3 and 711.0 cm^{-1} (Figure 4c), and at 283 cm^{-1} in the C–Si–C bending region. In the Si═O stretching region a D band at 1209.6 cm^{-1} and a M band at 1207.4 cm^{-1} appeared with

TABLE V: Isotopic Absorptions (cm^{-1}) Appearing on Irradiation of Argon Matrix Containing Dimethylsilane and Ozone

$(CH_3)_2SiH_2$		$(CH_3)_2SiD_2$		
$^{16}O_3$	$^{18}O_3$	$^{16}O_3$	$^{18}O_3$	ident
283	283	281	279	DS
616.2	616.2	514.2	514.2	DS
		668.6	668	
707.3	705.6			DS
711.0	708.5			DS
738.5	733.4			
757.2, 764.5	755.5, 763.4	621.1	609.6	DS
		758.4	758.9	
		769.7	768.6	
808.8	798.7			DS
819.4	810.3			DS
925	925	811	811	DS
		886.2 vs	875.2	DS
	1025.0		1025.0	carbinol
1207.4	1170.4	1202.3	1165.4	M
1209.6	1174.4	1209.6	1174.4	D
1212.1	1176.5			
1303.3	1303.3			CH_4
2111.0	2111.0	*a*	*a*	DS
3717.1	3705.2	2740.2	2723.5	DS

[a] Unresolved from Me_2SiD_2 precursor.

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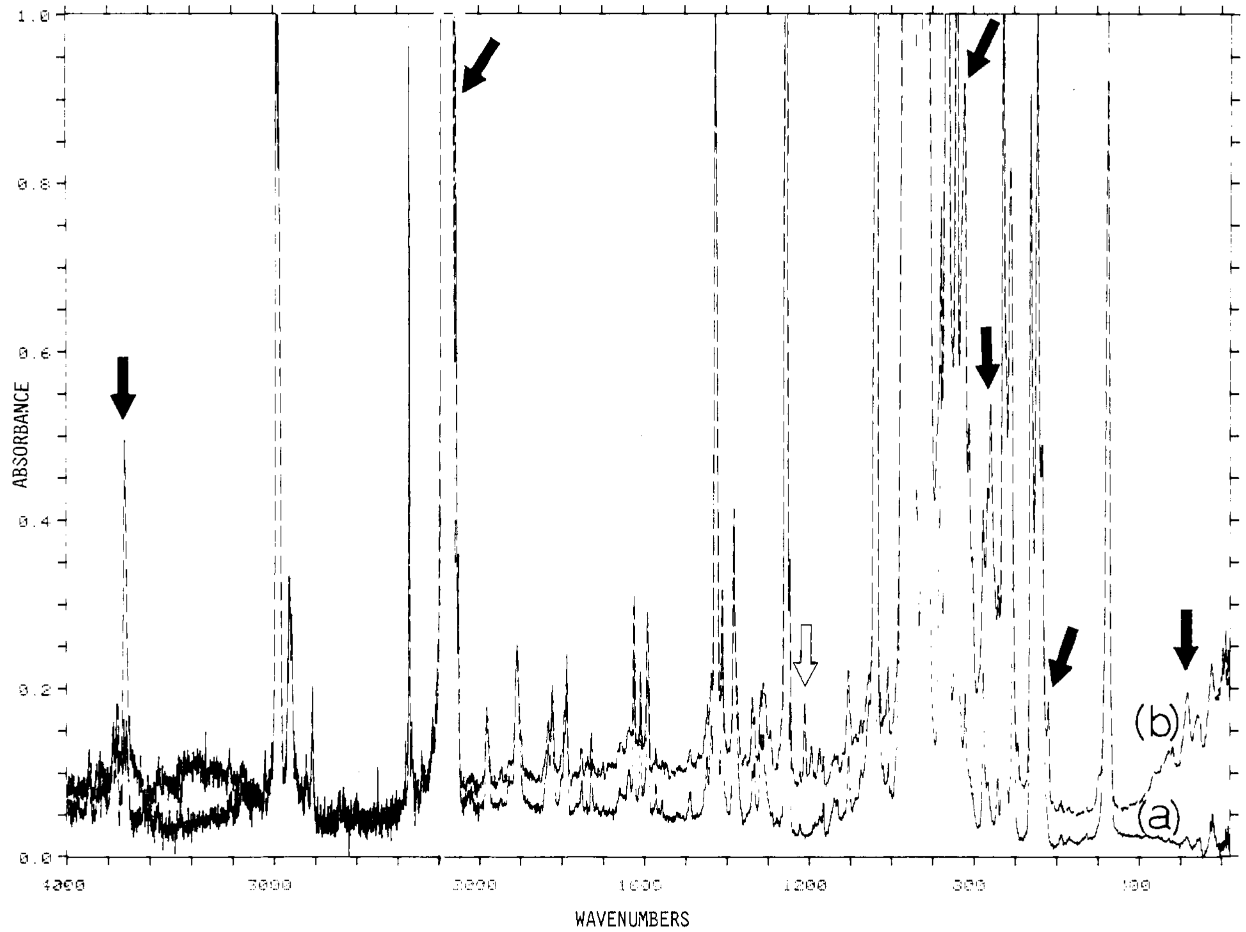

Figure 3. Infrared spectra of a sample of $Ar/Me_2SiH_2/^{16}O_3$ = 1200/3/4 in the 180–4000-cm^{-1} region (a) immediately after deposition at 14–17 K; (b) after irradiation C. Bold arrows indicate dimethylsilanol (DS) absorptions, and the light arrow shows a dimethylsilanone (D) band.

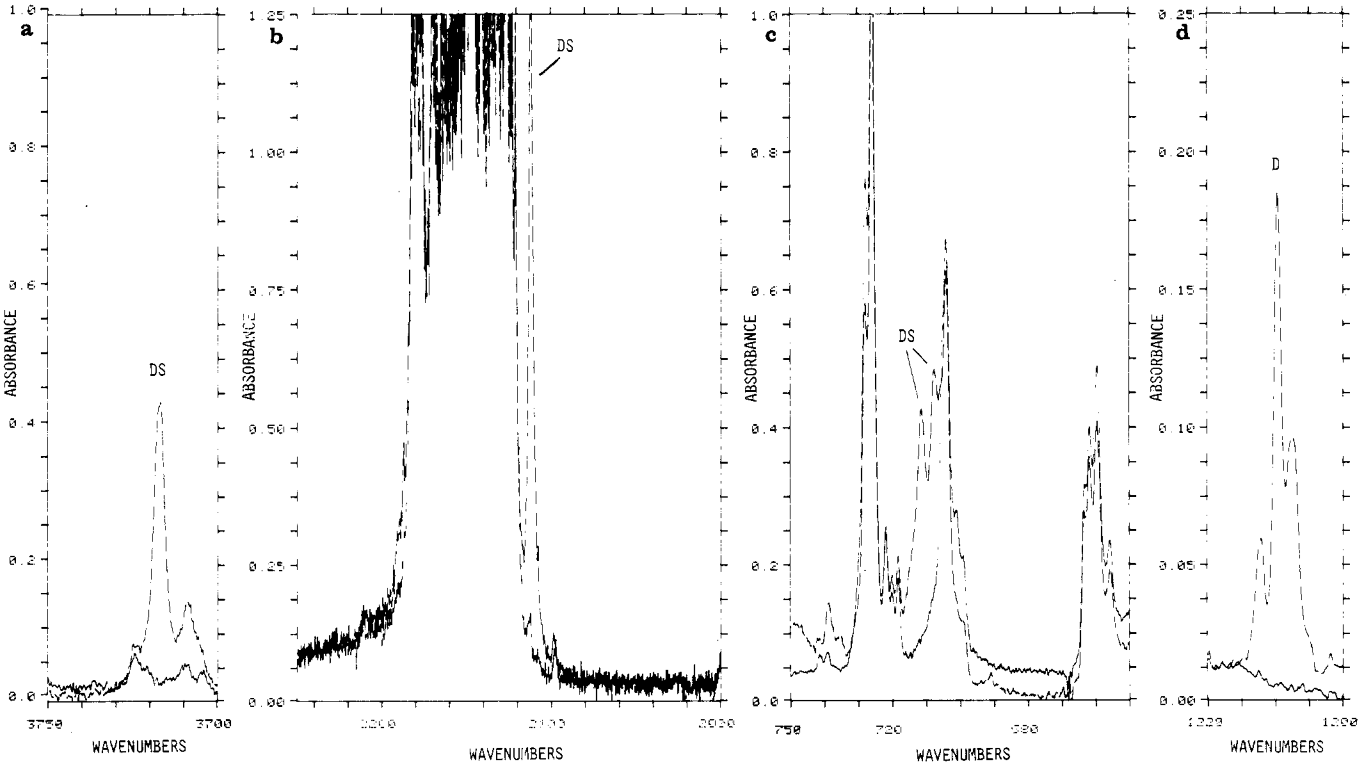

Figure 4. (a) Infrared spectra of a sample of $Ar/Me_2SiH_2/^{16}O_3$ = 2400/3/8 before (solid trace) and after (dashed trace) irradiation C at 14–17 K in the 3700–3750-cm^{-1} region. (b) Infrared spectra of a sample of $Ar/Me_2SiH_2/^{16}O_3$ = 2400/3/8 before (solid trace) and after (dashed trace) irradiation C at 14–17 K in the 2000–2250-cm^{-1} region. (c) Infrared spectra of a sample of $Ar/Me_2SiH_2/^{16}O_3$ = 2400/3/8 before (solid trace) and after (dashed trace) irradiation C at 14–17 K in the 650–750-cm^{-1} region. (d) Infrared spectra of a sample of $Ar/Me_2SiH_2/^{16}O_3$ = 400/1/1 before (solid trace) and after (dashed trace) irradiation C at 12 K in the 1160–1220-cm^{-1} region.

TABLE VI: Absorbances of Product Bands after Irradiations A, B, and C of Argon Matrix Containing Me$_3$SiH and ^{16}O$_3$

ν/cm^{-1}	A	B	C	ident
285.4	0.035	0.07	0.08	X
303.7	0.02	0.04	0.04	
346.9			0.015	
360.2	0.01	0.03	0.03	X
685		0.025	0.025	
729.6	0.15	0.35	0.42	X
745	0.06	0.12	0.14	
777.4	0.07	0.15	0.16	X
781.1	0.07	0.15	0.16	X
797	0.07	0.14	0.15	
899	*a*	*a*	*a*	X
1169.0		0.01	0.025	
1208.7		0.005	0.02	D
1305.6	0.015	0.03	0.04	CH$_4$
3715.4	0.06	0.11	0.15	X
3737 br	0.04	0.08	0.10	X

[a] Unresolved from parent Me$_3$SiH bands in survey scans.

TABLE VII: Isotopic Absorptions (cm^{-1}) Appearing on Irradiation of Argon Matrix Containing Trimethylsilane and Ozone

(CH$_3$)$_3$SiH		(CH$_3$)$_3$SiD		
^{16}O$_3$	^{18}O$_3$	^{16}O$_3$	^{18}O$_3$	ident
285.1	281.2	284.6	282.6	X
303.8	296	8		
346.9	342.7			
360.2	356.5	272.7	270.3	X
		613.2	609.4	
684 br	683 br			
729.7	726.2	591.6	587.2	X
745	745			
777.5, 781.0	761.8, 764.8	775.9	761.8	X
797 br	796 br			
899[a]	893[a]	895.4, 899.7 vs	887.3, 891.1	X
	1025.5		1025.1	carbinol
1169.0				
1208.7	1173.5	1208.7	1173.5	D
1305.6	1305.6			CH$_4$
3715.4	3703.8	2738.3	2721.8	X
3737	3726	2754	2737	X

[a] Intense shoulder on intense precursor band.

TABLE VIII: Positions and Absorbances of Product Bands after Irradiations B and C of Argon Matrix Containing Me$_4$Si, ^{16}O$_3$, and ^{18}O$_3$[a]

^{16}O$_3$			^{18}O$_3$
ν/cm^{-1}	B	C	ν/cm^{-1}
3637.1	0.01	0.03	3626.9
1165.9	0.03	0.095	1165.2
			1025.1
996.0	0.04	0.14	
753.5	0.095	0.29	753.3
334.6	0.03	0.08	328.7

[a] All of the above absorptions are assigned to the carbinol, Me$_3$SiCH$_2$OH.

irradiation B and grew in strongly with irradiation C (Figure 4d).

Me$_2$SiH$_2$ + ^{18}O$_3$. With ^{18}O$_3$, the DS band at 3717.1 cm^{-1} in the O–H stretching region was red-shifted to 3705.2 cm^{-1}. The D band at 1209.6 cm^{-1} in the Si–O stretching region was red-shifted to 1174.4 cm^{-1}, and the M band at 1207.4 cm^{-1} was red-shifted to 1170.4 cm^{-1}. The ^{18}O shifts of product bands are listed in Table V. With scrambled ^{16,18}O$_3$, only bands that were present in pure ^{16}O$_3$ and ^{18}O$_3$ experiments appeared.

Me$_2$SiD$_2$ + O$_3$. Samples of Me$_2$SiD$_2$ and ozone were codeposited, and photolysis product absorptions are listed in Table V. A very strong DS band at 886.2 cm^{-1} shifted to 875.2 cm^{-1} with ^{18}O. In the O–D stretching region, a DS band at 2740.2 cm^{-1} shifted to 2723.5 cm^{-1} with ^{18}O.

Me$_2$SiH$_2$ + O. Samples of dimethylsilane and discharged oxygen were codeposited for 8 h. New absorptions appeared that belong to species DS, and other product bands not present in Me$_2$SiH$_2$/O$_3$ experiments were also produced by vacuum-ultraviolet photolysis of Ar/Me$_2$SiH$_2$.[13]

Me$_3$SiH + ^{16}O$_3$. The matrix and gas-phase[15] infrared spectra of Me$_3$SiH were in good agreement. Exposure of Ar/Me$_3$SiH/^{16}O$_3$ samples to radiation produced new bands which are listed in Table VI along with their intensities during photolyses A–C. Figure 5a shows the survey infrared spectrum recorded with deposition, and Figure 5b shows the spectrum recorded with irradiation C. Two differences from MeSiH$_3$/O$_3$ and Me$_2$SiH$_2$/O$_3$ photolysis experiments were immediately apparent. First, two bands identified X appeared in the O–H stretching region at 3715.4 and 3737 cm^{-1} whereas only one band appeared in this region for MeSiH$_3$ and Me$_2$SiH$_2$. Second, the CH$_4$ band at 1305.6 cm^{-1} was produced by irradiations A and B as well as C whereas CH$_4$ appeared only with irradiation C for MeSiH$_3$ and Me$_2$SiH$_2$. In the Si=O stretching region the D band appeared with irradiation B and increased with irradiation C.

Me$_3$SiH + ^{18}O$_3$. A similar experiment was performed with Me$_3$SiH and ^{18}O$_3$. In the O–H stretching region the X bands at 3715.4 and 3737 cm^{-1} were shifted to 3703.8 and 3726 cm^{-1}, respectively. Also, the doublet at 777.5 and 781.0 cm^{-1} showed a large ^{18}O shift to 761.8 and 764.8 cm^{-1}. The D band at 1208.7 cm^{-1} shifted to 1173.5 cm^{-1}. The ^{18}O shifts of product bands are listed in Table VII.

Me$_3$SiD + O$_3$. Samples of Me$_3$SiD and ozone were photolyzed, and product absorptions are listed in Table VII. A very intense X doublet at 895.4 and 899.7 cm^{-1} was red-shifted to 887.3 and 891.1 cm^{-1} with ^{18}O. Two bands in the O–D stretching region at 2738.3 and 2754.4 cm^{-1} shifted to 2721.8 and 2737 cm^{-1}, respectively, with ^{18}O. Additionally, the strong X band at 729.7 cm^{-1} shifted to 591.6 cm^{-1} (H/D = 1.23), and the band at 285.1 cm^{-1} had very little deuterium shift appearing at 284.6 cm^{-1} with Me$_3$SiD.

Me$_3$SiH + O. Samples of trimethylsilane were codeposited with discharged oxygen. As with MeSiH$_3$ and Me$_2$SiH$_2$, a number of bands appeared which were also produced by vacuum-ultraviolet photolysis of Ar/Me$_3$SiH.[13] Other bands appeared at 284.8, 334.5, 730.9, 777.7, 804.0, 947.1, 1101, 1193, 1208.4, 1305.6, 1388.7, 3030, and 3712.1 cm^{-1}.

Me$_4$Si + ^{16}O$_3$. Exposure of Ar/Me$_4$Si/^{16}O$_3$ matrices to irradiation B produced new bands which are listed in Table VIII. These bands increased in intensity with irradiation C. The absence of a band in the Si=O stretching region is noteworthy. Analogous results were obtained with ^{18}O$_3$.

Discussion

Reaction products will be identified, and mechanisms for these reactions will be proposed. The new species produced here all require oxygen atoms from O$_3$ or discharged O$_2$. Since no additional bands were observed in any of the experiments with scrambled ^{16,18}O$_3$ that were not present in either ^{16}O$_3$ or ^{18}O$_3$ experiments, it appears that all of the photoproducts contain only one oxygen atom.

MeSiH$_3$ + O$_3$. The M band at 1207.6 cm^{-1}, in the Si=O stretching region, is identified as the Si=O stretch of methylsilanone, Me(H)Si=O. This is in keeping with its ^{18}O shift of 37.0 cm^{-1}, which is similar to the 43-cm^{-1} ^{18}O shift of the SiO diatomic molecule.[1] This identification is consistent with the small shift of 5.3 cm^{-1} when MeSiD$_3$ is employed. No other M bands were observed. This methylsilanone Si=O stretch at 1207.6 cm^{-1} comes close to the Si=O stretch of unsubstituted silanone. H$_2$SiO, at 1202 cm^{-1} in an argon matrix.[1] In fact, the weak B band at 1201.7 cm^{-1}, which appeared after irradiation C of matrices containing MeSiH$_3$ and ^{16}O$_3$, is identified as H$_2$SiO.

The MS bands are assigned to methylsilanol, MeSiH$_2$OH, as is now discussed. The MS band at 3716.0 cm^{-1} is clearly an O–H stretch since it has an ^{18}O shift of 11.8 cm^{-1}. Furthermore, the two very strong MS bands at 2127.4 and 2138.0 cm^{-1}, which show no ^{18}O shift, are appropriate for Si–H stretches since they come slightly to lower energy than the Si–H stretching absorptions of parent MeSiH$_3$. The very strong MS band at 718.5 cm^{-1} which

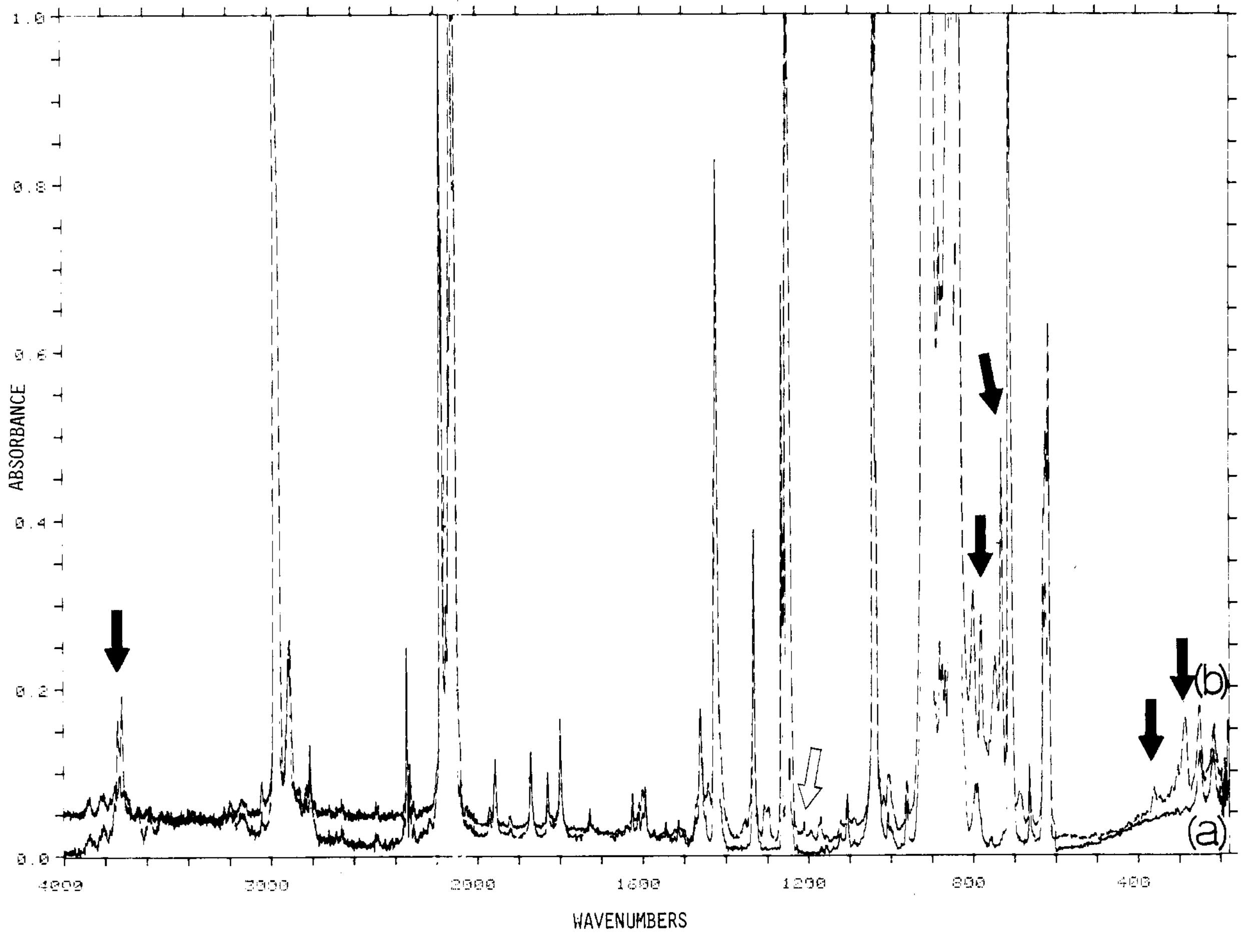

Figure 5. Infrared spectra of a sample of Ar/Me_3SiH/$^{16}O_3$ = 400/1/1 in the 180–4000-cm^{-1} region (a) immediately after deposition at 16–17 K; (b) after irradiation C. Bold arrows indicate species X absorptions, and the light arrow shows a dimethylsilanone (D) band.

has a small ^{18}O shift of 0.7 cm^{-1} is assigned to an Si–O–H bend since it comes close to the Si–O–H bend of hydroxysilylene at 723 cm^{-1}.[1,16] This is supported by its deuterium shift to 548 cm^{-1} (H/D = 1.311). The bands at 509.7 and 976.7 cm^{-1} also appear to belong to methylsilanol (MS) since their intensities bear a constant ratio to each other and to the intensity of the MS band at 718.5 cm^{-1}. The band at 976.7 cm^{-1} shows very little ^{18}O shift and a large $MeSiD_3$ shift to 753.7 cm^{-1} (H/D = 1.296). This band is most probably due to the H–Si–H bend since the H–Si–H bends of $MeSiH_2X$ compounds (X = Me, F, Cl, Br, I, and CN) have been observed in the 980–940-cm^{-1} region.[17] The MS band at 509.7 cm^{-1} which shows no measurable ^{18}O shift is probably due to the SiH_2 rock since such modes of the CH_3SiH_2X compounds have been observed in the 520–460-cm^{-1} region.[17] The band at 797.4 cm^{-1}, shifting to only 793.5 cm^{-1} with ^{18}O and 786.0 cm^{-1} with $MeSiD_3$, is assigned to a CH_3 rock. The very intense band at 876.4 cm^{-1} with $MeSiD_3$, which had a large shift of 17.0 cm^{-1} with ^{18}O, is assigned to the Si–O stretch of $MeSiD_2OD$. However, the ^{18}O shift of this band is still somewhat less than the ^{18}O shift of 27 cm^{-1} for the Si–O stretch of HSiOH[1,16] which occurs in the same frequency region. This is accounted for by mode mixing with SiD_2 and CH_3 deformation modes which come in the same frequency region. The Si–O stretch of fully protonated methylsilanol, $MeSiH_2OH$, was not observed, possibly because it is masked by the strong $MeSiH_3$ parent band centered by 870 cm^{-1}. There are two possible conformers of $MeSiH_2OH$ since the hydroxyl substitutent may be either trans or gauche to the methyl group as in ethanol,[18] and it is likely that both conformers are trapped in the argon matrix.

Si_2H_6 + O_3. The disilane–ozone product bands are assigned to silylsilanol, SiH_3SiH_2OH. The band at 3708.5 cm^{-1} belongs to an O–H stretch since it has an ^{18}O shift of 11.5 cm^{-1}. The bands at 961.6 and 950.6 cm^{-1} are likely both due to H–Si–H bending modes of the $-SiH_2-$ and $-SiH_3$ groups since they appear in this characteristic frequency region. The band at 950.6 cm^{-1} is probably due to the H–Si–H bending mode of the $-SiH_2-$ group since it has an ^{18}O shift of 2.2 cm^{-1} and the $-SiH_2-$ group is linked to the O atom. The band at 961.6 cm^{-1} which shows no ^{18}O shift but a large deuterium shift to 704.4 cm^{-1} (H/D = 1.365) with Si_2D_6 is due to a $-SiH_3$ deformation. The other two SiH_3 deformations are probably masked by parent Si_2H_6. The band at 855.0 cm^{-1} showing an ^{18}O shift of 2.9 cm^{-1} and a large deuterium shift to 637.4 cm^{-1} can be assigned to the $-SiH_2-$ twist. The band at 748 cm^{-1} shifting to 746 cm^{-1} with ^{18}O and to 556.9 cm^{-1} with deuterium is assigned to the Si–O–H bend coming in the same frequency region as the Si–O–H bend of HSiOH.[1,16] Finally, the band at 521.7 cm^{-1} is assigned to the SiH_2 rock since it comes close to the SiH_2 rock of the analogous compound, $MeSiH_2OH$, which was observed at 509.7 cm^{-1} (see earlier).

Me_2SiH_2 + O_3. The D band at 1209.6 cm^{-1} which shifted 35.2 cm^{-1} with ^{18}O is assigned to the Si=O stretch of dimethylsilanone, $Me_2Si{=}O$, which is near the Si=O stretch of $H_2Si{=}O$ at 1202 cm^{-1}.[1] Furthermore, the band at 1209.6 cm^{-1} shows no deuterium shift when Me_2SiD_2 is employed. The Si=O stretching fundamental of Me_2SiO has been previously observed[4] at 1204 cm^{-1}; however, the discrepancy is almost certainly accounted for by the sensitivity of this fundamental to neighboring byproduct molecules. The M band at 1207.4 cm^{-1} is identified as the Si=O stretch of Me(H)Si=O as it shifts 37.0 cm^{-1} with ^{18}O.

Species DS has bands with isotopic shifts appropriate for identification as dimethylsilanol. The band at 3717.1 cm^{-1} shifting to 3705.2 cm^{-1} with ^{18}O is the O–H stretch, and this comes close to the O–H stretch of methylsilanol at 3716.0 cm^{-1}. The very intense band at 2111.0 cm^{-1} showing no ^{18}O shift belongs to the

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

(17) Ebsworth, E. A. V.; Onyszchuk, M.; Sheppard, N. *J. Chem. Soc.* **1958**, 1453.

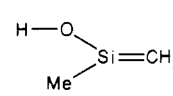
(18) Barnes, A. J.; Hallam, H. E.; *Trans. Faraday Soc.* **1970**, *66*, 1932.

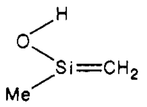
Si–H stretch. The doublet at 707.3 and 711.0 cm^{-1} shifting to 705.6 and 708.5 cm^{-1} with ^{18}O is assigned to the Si–O–H bend for two reasons. First, the small observed ^{18}O shift of 1.7 cm^{-1} (or 2.5 cm^{-1}) is approximately the same magnitude as the ^{18}O shift of 2.6 cm^{-1} observed for this mode of HSiOH.[16] Second, this band appears in the same frequency region as the Si–O–H bend of HSiOH[1,16] and methylsilanol, MeSiH$_2$OH (see earlier). When Me$_2$SiD$_2$ was employed, the counterpart of this band was not observed, but it is likely that it is shifted underneath the strong Me$_2$SiD$_2$ parent band which masked the 540–560-cm^{-1} region. The weak DS band at 283 cm^{-1}, exhibiting very little ^{18}O or D shift, is assigned to the C–Si–C skeletal bend. This fundamental is expected here since the C–Si–C bend of Me$_2$Si(OH)$_2$ in a KBr pellet has recently been observed at 250 cm^{-1}.[13] The band at 616.2 cm^{-1} which has no ^{18}O shift also belongs to DS. It shifts down to 514.2 cm^{-1} with Me$_2$SiD$_2$ bearing a ratio of 1.20 with its protonated counterpart. It is possibly due to a mixture of a methyl rock and a H–Si–C bend since, in both Me$_2$SiH$_2$/O$_3$ and Me$_2$SiD$_2$/O$_3$ experiments, this DS band is a lower energy satellite of the dimethylsilane ν_{21} fundamental[15] which is a mixture of a methyl rock and SiH$_2$ wag. Likewise the very strong DS band at 925 cm^{-1} which has no ^{18}O shift occurs as a higher energy satellite of the ν_{19} fundamental of Me$_2$SiH$_2$ which is also a mixture of a methyl rock and SiH$_2$ wag.[15] With Me$_2$SiD$_2$, the DS band at 925 cm^{-1} shifts down to 811 cm^{-1} (H/D = 1.14) occurring as a higher energy satellite of the ν_{19} parent Me$_2$SiD$_2$. Therefore, it is likely that the DS band at 925 cm^{-1} is also due to a mixture of methyl rock and H–Si–C bend. The doublet of bands at 757.2 and 764.5 cm^{-1} shifting to 755.5 and 763.4 cm^{-1} with ^{18}O also belong to DS. It appears that this doublet is red-shifted to 612.1 cm^{-1} (H/D = 1.24) in Me$_2$SiD$_2$ + ^{16}O$_3$ experiments (2.5 cm^{-1} ^{18}O shift). This suggests it as a possible candidate for the H–Si–O bend. The band at 819.4 cm^{-1} exhibiting a considerable shift of 9.1 cm^{-1} with ^{18}O is possibly due to the CH$_3$ symmetric rock; however, no firm assignment can be made since its deuterium counterpart was not observed. The very strong band at 886.2 cm^{-1} with Me$_2$SiD$_2$, which had an ^{18}O shift of 11.0 cm^{-1}, is assigned to the Si–O stretch of Me$_2$SiDOD since it has the largest ^{18}O shift of all the bands observed in this frequency region and it comes close to the band at 876.4 cm^{-1} which was assigned to the Si–O stretch of MeSiD$_2$OD (see earlier). The Si–O stretch of fully protonated dimethylsilanol, Me$_2$SiHOH, was not observed, possibly because it is masked by the strong Me$_2$SiH$_2$ parent peak absorbing in the 860–870-cm^{-1} region. As with MeSiH$_2$OH there are two possible conformers of Me$_2$SiHOH since the OH group may be either trans or gauche to the silyl hydrogen. This is possibly the reason why the Si–O–H bend appears as a doublet at 707.3 and 711.0 cm^{-1}, the individual components of which do not have exactly the same ^{18}O shift.

Me$_3$SiH + O$_3$. The D band at 1208.7 cm^{-1} is assigned to the Si=O stretch of dimethylsilanone, Me$_2$SiO, in close proximity to a CH$_4$ byproduct molecule. This identification is made on the basis of the ^{18}O isotopic shift of 35.2 cm^{-1} which is identical with the ^{18}O shift observed for the Si=O stretch of Me$_2$SiO product in Me$_2$SiH$_2$/O$_3$ experiments. Further support for the identification of the 1208.7-cm^{-1} band as the Si=O stretch of Me$_2$SiO was the lack of an isotopic shift when Me$_3$SiD was employed. The band at 1305.6 cm^{-1} which grows in with the 1208.7-cm^{-1} absorption is due to the CH$_4$ byproduct. It is notable that the Si=O stretch of Me$_2$SiO from Me$_3$SiH and O$_3$ precursors comes 0.9 cm^{-1} lower than the Si=O stretch of Me$_2$SiO from Me$_2$SiH$_2$ and O$_3$ precursors. This discrepancy is probably due to the perturbing influence of the neighboring CH$_4$ molecule which was not present in dimethylsilane experiments.

The other product bands (see Table VI) are clearly not due to trimethylsilanol, Me$_3$SiOH.[19] This was an expected product since methylsilanol, MeSi$_2$OH, and dimethylsilanol, Me$_2$SiHOH, were formed in high yield in parallel MeSiH$_3$/O$_3$ and Me$_2$SiH$_2$/O$_3$ photolysis experiments. In order to determine matrix shifts for Me$_3$SiOH bands compared to the gas phase, a sample of Me$_3$SiOH was prepared[20] and its matrix infrared spectrum recorded. There was good agreement between matrix and gas-phase infrared spectra of Me$_3$SiOH.[19] Therefore, it can be concluded that Me$_3$SiOH was not a product of the matrix photolysis of Me$_3$SiH and O$_3$. Finally, the 1305.6-cm^{-1} methane band grows in gradually throughout the irradiation sequence A–C. Therefore, CH$_4$ is produced in the photolysis of Me$_3$SiH/O$_3$, which also rules out the formation of Me$_3$SiOH from Me$_3$SiH and O$_3$.

The identification of species X can now be considered. The broad band at 3737 cm^{-1} shifting to 3726 cm^{-1} and the band at 3715.4 cm^{-1} shifting to 3703.8 cm^{-1} with ^{18}O are both appropriate for O–H stretches. The very strong band at 729.7 cm^{-1} which shifts to 726.2 cm^{-1} with ^{18}O is assigned to an Si–O–H bend. This assignment is supported by the deuterium shift to 591.6 cm^{-1} (H/D = 1.23) with Me$_3$SiD, which indicates a large percentage of hydrogen character in this mode. The band at 360.2 cm^{-1}, which shifts down to 356.5 cm^{-1} with ^{18}O and shows a large shift to 284.6 cm^{-1} (H/D = 1.32) with Me$_3$SiD is almost certainly due to a H–O–Si–C torsion, since this mode involves the H atom which undergoes isotopic substitution. The doublet at 777.5 and 781.0 cm^{-1}, showing an ^{18}O shift of 16.0 cm^{-1}, the largest observed in this spectrum, is assigned to an Si–O stretch. This assignment is made on account of the high percentage oxygen character of this mode even though a pure Si–O bond stretch should show an ^{18}O shift of approximmately 28 cm^{-1} in this frequency region. It is striking that this Si–O stretching frequency is considerably lower than the Si–O stretches observed for MeSiD$_2$OD and Me$_2$SiDOD (see above) and the Si–O stretch of gas-phase Me$_3$SiOH, which was reported at 915 cm^{-1}.[19] The very strong band at 899 cm^{-1}, which is shifted to 893 cm^{-1} with ^{18}O and shows very little deuterium shift, is most probably due to a mode involving Si=C stretching and methyl rocking character since these modes, which occur in this frequency region, are often very intense. The band at 285.1 cm^{-1} shifting to 281.2 cm^{-1} with ^{18}O and showing very little deuterium shift may be due to a C–Si–C bend as it comes in this particular frequency region. It appears quite possible that species X is the enol isomer of dimethylsilanone, namely, the substituted silaethylene, Me(HO)Si=CH$_2$, which has the reagent stoichiometry plus O minus CH$_4$. The infrared data are consistent with such a structure. Perhaps the two hydroxyl stretches which are observed at 3715.4 and 3737 cm^{-1} are due to the two distinct isomeric structures





No Me$_3$SiOH was detected from the reaction of O atoms with Me$_3$SiH either. However, a band appeared at 1208.4 cm^{-1} which is due to the Si=O stretch of Me$_2$SiO as it comes very close to the Me$_3$SiH/O$_3$ photolysis product. Furthermore, the yield of Me$_2$SiO in the discharge experiment was approximately 5 times that of the ozone photolysis experiments. Other weak features which have not been identified appeared at 730.0, 736.5, 777.7, 804.0, 947.1, 1100.7, and 1193 cm^{-1} (broad) in the discharge experiment.

Me$_4$Si + O$_3$. It seems likely that there is O atom insertion into a C–H bond of this fully methyl substituted silane to give a carbinol. The band at 1025.1 cm^{-1} in the Me$_4$Si/^{18}O$_3$ experiment is likely due to the C–^{18}O stretch with the C–^{16}O stretch in the Me$_4$Si/^{16}O$_3$ experiment almost certainly masked by the strong ^{16}O$_3$ band at 1040 cm^{-1}.[7] This C–O stretching frequency comes very close to the C–O stretch of CH$_3$OH in solid argon at 1034.0 cm^{-1} which shifted to 1008.2 cm^{-1} with ^{18}O.[21] In the hydroxyl region the band at 3637.1 cm^{-1} (10.2-cm^{-1} with ^{18}O) is clearly the O–H stretch of this carbinol. It is distinct from the O–H

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(19) Rouviere, J.; Tabacik, V.; Fleury, G. *Spectrochim. Acta, Part A* **1973**, *29A*, 229.

(20) See Sauer, R. O. *J. Am. Chem. Soc.* **1944**, *66*, 1707 for the preparation details of Me$_3$SiOH. The ^{1}H NMR spectrum contained two peaks having relative intensities of 9.6:1, which is close to the expected ratio of 9:1.

(21) Barnes, A. J.; Hallam, H. E. *Trans. Faraday Soc.* **1970**, *66*, 1920.

product stretches in $MeSiH_3$, Me_2SiH_2, and Me_3SiH experiments since these silanol O–H stretches have higher frequencies in the 3700-cm^{-1} region. The band in the low-frequency region at 334.6 cm^{-1} (^{18}O shift of 5.9 cm^{-1}) most probably belongs to the Si–C–O bend of the carbinol. The strong band at 753.5 cm^{-1} (^{18}O shift of 0.2 cm^{-1}) is possibly due to the $-CH_2-$ rock of the $-SiCH_2OH$ group. In addition, the band at 1165.9 cm^{-1} (^{18}O shift of 0.7 cm^{-1}) may well be due to the H–C–H bend of the methylene group. Assignment of the product band at 996.0 cm^{-1} is not attempted as its ^{18}O shift was not determined, probably owing to masking by ν_3 of $^{18}O_3$.

Mechanisms. Formation of the alcohol products discussed in the foregoing section can be envisioned by oxygen atom insertion into either a Si–H or, in the case of Me_4Si, a C–H bond. The insertion of O atoms into Si–H bonds has been reported in similar studies with SiH_4[1] and $SiHCl_3$.[2] Likewise, oxygen atoms insert into C–H bonds of CH_4 to give CH_3OH[22] and C_2H_4 to give vinyl alcohol.[23] In the present study with methyl-substituted silanes, the O atom has a choice of insertion into a Si–H bond or a C–H bond (except for Me_4Si). These experiments indicate that O atom insertion into a Si–H bond is clearly favored. For example, with $MeSiH_3$, which has three Si–H bonds and three C–H bonds, methylsilanol was formed in high yield and no carbinol was detected. However, in photolysis experiments with Me_3SiH, which has one Si–H bond and nine C–H bonds, a trace of the carbinol was produced in addition to the major product which has been tentatively identified as $H_2C{=}Si(OH)Me$. These observations are consistent with a thermodynamic preference for O atom insertion into a Si–H (D[Si–H] $\sim$ 90 kcal mol^{-1}) rather than a C–H bond (D[C–H] $\sim$ 100 kcal mol^{-1}). In spite of this thermodynamic preference to form the silanol rather than the carbinol, a small amount of carbinol was formed in Me_3SiH/O_3 photolysis experiments because it is kinetically favored.

(*i*) *Substituted Methylsilane + O Atom Discharge Experiments.* $MeSiH_3$/O atom experiments contrasted rather strikingly with SiH_4/O atom discharge experiments.[1] The latter gave little evidence for silanol, H_3SiOH, but hydroxysilylene, HSiOH, was produced in high yield.[1] On the other hand, methylsilanol, $MeSiH_2OH$, was formed in high yield, and there was no evidence for the silylenes HSiOH or MeSiOH in $MeSiH_3$/O atom discharge experiments. It seems likely that O atom insertion into an Si–H bond of SiH_4 produces an energized silanol molecule which eliminates molecular hydrogen to give HSiOH.

$$SiH_4 + O(^3P) \rightarrow [H_3SiOH]^* \rightarrow HSiOH + H_2$$

However, the energized methylsilanol molecule, produced by O atom insertion into an Si–H bond of $MeSiH_3$, does not dissociate as rapidly, and the excess energy relaxes by intramolecular vibrational energy transfer and is quenched by the matrix.

$$MeSiH_3 + O(^3P) \rightarrow [MeSiH_2OH]^* \rightarrow MeSiH_2OH$$

It is presumed that $[H_3SiOH]^*$ dissociates more readily than $[MeSiH_2OH]^*$ because the excess energy is distributed over fewer vibrational modes. Me_2SiHOH is similarly produced in Me_2SiH_2 + O atom experiments.

$$Me_2SiH_2 + O(^3P) \rightarrow [Me_2SiHOH]^* \rightarrow Me_2SiHOH$$

In Me_3SiH + O atom discharge experiments the Me_2SiO product is almost certainly produced via an energized Me_3SiOH intermediate.

$$Me_3SiH + O(^3P) \rightarrow [Me_3SiOH]^* \rightarrow Me_2SiO + CH_4$$

(*ii*) *Substituted Methylsilane + Ozone Photolysis Experiments.* The mechanism of formation of the methylsilanones, which occurs under full-arc (220 < λ < 1000 nm) conditions, most probably involves H_2 or CH_4 molecular elimination from the vibrationally excited methylsilanols. Both H_2 and CH_4 elimination may occur as the Si–H and Si–C bond energies are nearly equivalent.[24] However, the relative yields of the dimethyl-substituted methyl-substituted, and unsubstituted silanones demonstrate that Si–H cleavage is favored.

$$Me_3SiH + O(^1D) \rightarrow [Me_3SiOH]^* \rightarrow Me_2SiO + CH_4$$

$$Me_2SiH_2 + O(^1D) \rightarrow [Me_2SiHOH]^* \rightarrow Me_2SiO + H_2$$

$$\rightarrow Me(H)SiO + CH_4$$

$$MeSiH_3 + O(^1D) \rightarrow [MeSiH_2OH]^* \rightarrow Me(H)SiO + H_2$$

$$\rightarrow H_2SiO + CH_4$$

When the incident radiation is less energetic (290 < λ < 1000 nm), $MeSiH_2OH$ and Me_2SiHOH are not born with sufficient excess energy to undergo unimolecular dissociation.

$$MeSiH_3/O_3 + h\nu\ (290 < \lambda < 1000\ \text{nm}) \rightarrow [MeSiH_2OH]^* + O_2 \rightarrow MeSiH_2OH + O_2$$

$$Me_2SiH_2/O_3 + h\nu\ (290 < \lambda < 1000\ \text{nm}) \rightarrow [Me_2SiHOH]^* + O_2 \rightarrow Me_2SiHOH + O_2$$

Failure to observe trimethylsilanol, Me_3SiOH, in Me_3SiH/O_3 photolysis strikingly contrasts the formation of $MeSiH_2OH$ and Me_2SiHOH in the respective $MeSiH_3$ and Me_2SiH_2 experiments. Me_3SiH/O_3 photolysis probably proceeds via $[Me_3SiOH]^*$, however, to give $H_2C{=}S(OH)Me$, an isomer of Me_2SiO.

$$Me_3SiH/O_3 + h\nu\ (290 < \lambda < 1000\ \text{nm}) \rightarrow [Me_3SiOH]^* + O_2 \rightarrow H_2C{=}Si(OH)Me + CH_4 + O_2$$

It appears likely that $[Me_3SiOH]^*$ may eliminate methyl radical more readily than excited methyl- or dimethylsilanols owing to increased stability of the more highly substituted silyl free radical. Once produced, CH_3 can then abstract the hydroxyl hydrogen or a methyl hydrogen to give the silanone or its enol form. Me_2SiO is probably more thermodynamically stable than its enol isomer, $H_2C{=}Si(OH)Me$, since the similar Me(H)SiO molecule has been calculated to be 21.2 kcal mol^{-1} lower in energy than its enol isomer, $H_2C{=}SiHOH$, at the MP3/6-31G* level.[25] The formation and trapping of $H_2C{=}Si(OH)Me$ in spite of its higher energy with respect to Me_2SiO is reasonable, though, as long as the barrier to isomerization via intramolecular rearrangement is high. Such is the case with vinyl alcohol, which is less thermodynamically stable than the acetaldehyde isomer, but nevertheless vinyl alcohol has been produced by photolysis in solid argon matrices.[23]

The Si_2H_6/O_3 photolysis experiments *exclusively* gave insertion into a Si–H bond and the silylsilanol product; disiloxane was not detected. This may be surprising owing to the long, weak Si–Si bond.

Conclusions

Methyl- and dimethylsilanols have been observed from O atom reactions and O_3 photolysis (290 < λ < 1000 nm) in argon matrices containing $MeSiH_3$ and Me_2SiH_2, respectively. Similarly, in Si_2H_6/O_3 photolysis experiments, product bands were observed which are identified as silylsilanol, SiH_3SiH_2OH. The O–H stretching frequency of these silanols appears in the 3700-cm^{-1} region close to the O–H stretches of Cl_3SiOH (3639.5 cm^{-1} in solid argon)[2] and Me_3SiOH (3737 cm^{-1} in gas phase).[19]

Me_3SiOH was not identified in the reactions of oxygen atoms with Me_3SiH; however, in Me_3SiH/O atom discharge experiments, Me_2SiO was produced. When argon matrices containing Me_3SiH/O_3 were irradiated in the region 290 < λ < 1000 nm, a new set of bands appeared that have tentatively been assigned to $H_2C{=}Si(OH)Me$, the enol isomer of Me_2SiO.

Full mercury arc irradiation (220 < λ < 1000 nm) of argon matrices containing Me_3SiH/O_3 gave dimethylsilanone, Me_2SiO.

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Similarly, Me_2SiO and $Me(H)SiO$ were observed in Me_2SiH_2/O_3 experiments, and $Me(H)SiO$ and H_2SiO were produced in $MeSiH_3/O_3$ experiments. Both H_2 and CH_4 eliminate from excited methylsilanols cleaving Si–H or Si–C bonds; however, the relative yields of the silanone products show that Si–H cleavage is favored. No silanones were observed in similar Me_4Si/O_3 experiments, but new bands appeared that likely belong to the carbinol resulting from O atom insertion into a C–H bond of Me_4Si.

The argon matrix is a convenient vehicle for first-step oxidation of reactive compounds like the silanes with infrared spectroscopic identification of the products.

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Registry No. O_3, 10028-15-6; $MeSiH_3$, 992-94-9; $Me(H)Si{=}O$, 43435-60-5; $^{18}O_3$, 21424-26-0; H_2SiO, 22755-01-7; $MeSiH_2OH$, 111935-69-4; $MeSiD_3$, 1066-43-9; $MeSiD_2OD$, 111935-70-7; SiH_3SiH_2OH, 87963-93-7; Si_2H_6, 1590-87-0; Me_2SiH_2, 1111-74-6; $Me_2Si{=}O$, 47956-45-6; Me_2SiD_2, 1066-41-7; Me_2SiHOH, 5906-76-3; Me_2SiDOD, 111935-71-8; Me_3SiH, 993-07-7; Me_3SiD, 18026-91-0; $Me(HO)Si{=}CH_2$, 111935-72-9; Me_4Si, 75-76-3; Me_3SiCH_2OH, 3219-63-4; Si_2D_6, 13537-08-1; O, 17778-80-2.

A Quasi-Classical Approximation for Autocorrelation Functions

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A quasi-classical approximation is presented for the calculation of time autocorrelation functions of properties of bound molecular systems. In this treatment, classical motion is restricted to quantized invariant tori on a discretized energy shell. The dynamics on these tori is obtained by the adiabatic switching technique. When applied to the Henon-Heiles system, the quasi-classical approximation is sometimes found to yield significantly better agreement with the quantum results than that obtained from conventional classical calculations.

I. Introduction

Time correlation functions are of central importance for the description of motion in isolated, molecular systems. Somewhat different versions of such functions are used to determine optical spectra,[1-3] to calculate probabilities for transitions among internal states,[4-6] to formulate stochastic theories of intramolecular dynamics,[7] and to detect the presence of chaotic[8] or ergodic behavior.[9-13]

Since a full quantum mechanical calculation of such functions is usually not feasible, it is desirable to develop various classical approximations. The goal of this paper is to present one such approximation that is sometimes capable of yielding good agreement with the exact quantum results.

The original motivation for this work came from an earlier comparison[10] between quantum and analogous classical autocorrelation functions for the Henon–Heiles[14] system. Although the quantum and classical quantities were generally found to agree well when the energy of the system was high, they were sometimes found to disagree significantly when the energy of the system was lower. The explanation offered for these discrepancies implied that the agreement could be improved if the classical calculations were confined to a set of discrete invariant tori corresponding to states contributing to the quantum dynamics. This idea forms the basis for the present work.

We organize the remainder of this paper as follows. In section II, we describe our basic method for simulating quantum correlation functions. In section III, we present more details about the application of this technique to the Henon-Heiles system. In section IV we compare autocorrelation functions computed by the present method to exact quantum and conventional classical autocorrelation functions. Finally, in section V, we make some concluding remarks.

II. Approach

The time–autocorrelation functions we explore here are of the form

$$C_A(t) = \mathrm{Tr}[\rho^\sigma(E - \hat{\mathcal{H}})\hat{A}(t)^\dagger\hat{A}]/\mathrm{Tr}[\rho^\sigma(E - \hat{\mathcal{H}})\hat{A}^\dagger\hat{A}] \quad (1)$$

where $\hat{A}$ is a quantum operator, $\hat{A}(t)$ is this operator at time t in the Heisenberg representation, and $\hat{\mathcal{H}}$ is the Hamiltonian for the system. The quantity ρ^δ is a "broadened delta function" which projects onto states in the energy shell of half-width δ about energy E. Specifically, we use the expression

$$\rho^\sigma(E - \hat{\mathcal{H}}) = \exp[-(E - \hat{\mathcal{H}})^2/2\sigma^2] \quad (2)$$

although others may be applied.

The form of $C_A(t)$ defined above is general enough to be useful in many physical cases. For example, if σ is chosen to be very

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