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Spectroscopic Studies of Dialkylaluminum Alkoxides and the Trialkylaluminum-Ether Complex. II. Assignments of Observed Frequencies

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The polarization data on the Raman lines of $Al(CH_3)_3 \cdot (CH_3)_2O$, $[Al(CH_3)_2OCH_3]_3$, $[Al(C_2H_5)_2OCH_3]_3$, and $[Al(C_2H_5)_2OC_2H_5]_2$ have been obtained in the 3100—130 cm^{-1} region. Most of the infrared absorption bands and Raman lines of these four compounds in the skeletal vibration region (720—130 cm^{-1}) have been tentatively assigned with the aid of these polarization data and on the assumption that the symmetries of these four compounds are as given in the previous paper. The Raman spectra of $Al(CH_3)_3 \cdot (CD_3)_2O$, $[Al(CH_3)_2OCD_3]_3$, and $[Al(C_2H_5)_2OC_2D_5]_2$ have been measured in the 3100—130 cm^{-1} region. Most of the infrared absorption bands and Raman lines of $Al(CH_3)_3 \cdot (CH_3)_2O$, $[Al(CH_3)_2OCH_3]_3$, $[Al(C_2H_5)_2OCH_3]_3$, and $[Al(C_2H_5)_2OC_2H_5]_2$ in the CH-stretching region (3100—2700 cm^{-1}) have been assigned with the aid of the spectroscopic data of the above-mentioned partly-deuterated substances.

In a previous paper,[1] the author showed that dimethylaluminum methoxide $[Al(CH_3)_2OCH_3]_3$ and diethylaluminum methoxide $[Al(C_2H_5)_2OCH_3]_3$ take trimeric structures with the D_{3h} symmetry, that diethylaluminum ethoxide $[Al(C_2H_5)_2OC_2H_5]_2$ takes a dimeric structure with the V_h symmetry and that the trimethylaluminum-dimethyl ether complex, $Al(CH_3)_3 \cdot (CH_3)_2O$, takes the structure with the C_s symmetry; these assignments were made by comparing the infrared and Raman spectra of these four compounds in the skeletal vibration region (720—300 cm^{-1}). (The

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[1] R. Tarao, This Bulletin, **39**, 725 (1966).

assignments of the observed frequencies were impossible at that time except for $Al(CH_3)_3 \cdot (CH_3)_2O$.²⁾ The present paper will describe the results of the qualitative measurements of the degree of the depolarization of the Raman lines of these four compounds. The Raman spectra of three partly-deuterated substances, $Al(CH_3)_3 \cdot (CD_3)_2O$, $[Al(CH_3)_2OCD_3]_3$, and $[Al(C_2H_5)_2OC_2D_5]_2$, will also be measured. The tentative assignments for the infrared absorption bands and Raman lines of $Al(CH_3)_3 \cdot (CH_3)_2O$, $[Al(CH_3)_2OCH_3]_3$, $[Al(C_2H_5)_2OCH_3]_3$, and $[Al(C_2H_5)_2OC_2H_5]_2$ will be made with the aid of the polarization data and the spectroscopic data of the abovementioned partly-deuterated substances.

Experimental

$Al(CH_3)_3 \cdot (CH_3)_2O$, $[Al(CH_3)_2OCH_3]_3$, $[Al(C_2H_5)_2OCH_3]_3$, and $[Al(C_2H_5)_2OC_2H_5]_2$ were prepared by the method described in the previous paper.¹⁾ Deuterated materials (dimethyl-d_6-ether, methanol-d_3, and ethanol-d_5) were purchased from the Volk Co. (isotopic purity > 99%). $Al(CH_3)_3 \cdot (CD_3)_2O$ was prepared by the reaction of trimethylaluminum with dimethyl-d_6-ether, b. p. 72—73°C/42 mmHg. $[Al(CH_3)_2OCD_3]_3$ was prepared by the reaction of trimethylaluminum with methanol-d_3, b. p. 70.5—72°C/3.5 mmHg. $[Al(C_2H_5)_2OC_2D_5]_2$ was prepared by the reaction of triethylaluminum with ethanol-d_5, b. p. 114—116°C/12 mmHg. The Raman spectra were measured by the method described in the previous paper.¹⁾ The polarization data of Raman lines

TABLE I. THE NUMBER OF SKELETAL NORMAL VIBRATIONS OF $Al(CH_3)_3 \cdot (CH_3)_2O$ (C_s)

Mode of vibration	A′	A″	Total
Activity IR	+	+	
Activity Raman	+	+	
AlC_3 stretching	2	1	3
AlC_3 deformation	2	1	3
AlC_3 rocking	1	1	2
AlC_3 torsion		1	1
AlO stretching	1		1
CO stretching	1	1	2
OC_2 scissors	1		1
OC_2 wagging	1		1
OC_2 rocking		1	1
Total	9	6	15

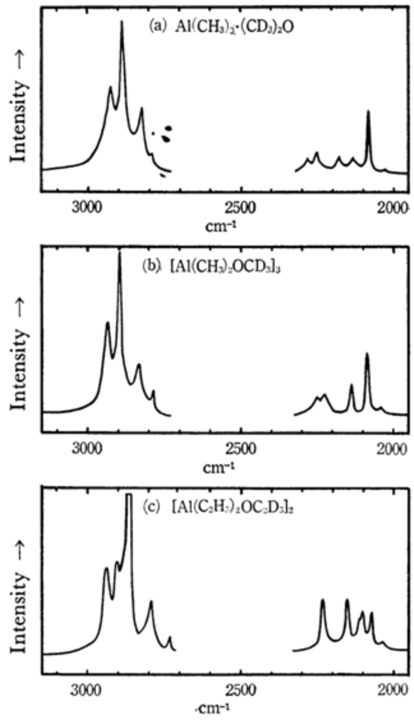

Fig. 1. The Raman spectra of partly deuterated substances in the CH and CD stretching region.

TABLE II. THE NUMBER OF SKELETAL NORMAL VIBRATIONS OF $[Al(CH_3)_2OCH_3]_3$ AND $[Al(C_2H_5)_2OCH_3]_3$*¹ (D_{3h})

Mode of vibration	A_1'	A_2'	E′	A_1''	A_2''	E″	Total
Activity IR	−	−	+	−	+	−	
Activity Raman	+	−	+	−	−	+	
AlC_2 stretching	1		1		1	1	4
AlC_2 scissors	1		1				2
Ring stretching	1	1	2				4
Ring in-plane deformation	1		1				2
Ring out-of-plane deformation					1	1	2
AlC_2 wagging		1	1				2
AlC_2 rocking					1	1	2
AlC_2 twisting				1		1	2
CO stretching	1		1				2
CO in-plane bending		1	1				2
CO out-of-plane bending					1	1	2
Total	5	3	8	1	4	5	26

*¹ For $[Al(C_2H_5)_2OCH_3]_3$, C_2H_5 group is treated as a single particle to simplify the discussion.

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2) S. Takeda and R. Tarao, ibid., **38**, 1567 (1965).

TABLE III. THE NUMBER OF SKELETAL NORMAL VIBRATIONS OF $[Al(C_2H_5)_2OC_2H_5]_2$[*1] (V_h)

Mode of vibration	A_g	A_u	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}	Total
Activity IR	−	−	−	+	−	+	−	+	
Activity Raman	+	−	+	−	+	−	+	−	
AlC_2 stretching	1			1	1			1	4
AlC_2 scissors	1							1	2
Ring stretching	1		1			1			3
Ring deformation	1							1	2
AlC_2 wagging			1			1			2
AlC_2 rocking				1	1				2
AlC_2 twisting		1					1		2
Ring puckering				1					1
CO stretching	1					1			2
CO in-plane bending			1					1	2
CO out-of-plane bending				1			1		2
Total	5	1	3	4	2	3	2	4	24

[*1] C_2H_5 group is treated as a single particle to simplify the discussion.

TABLE IV. OBSERVED FREQUENCIES OF $Al(CH_3)_3\cdot(CH_3)_2O$ AND $Al(CH_3)_3\cdot(CD_3)_2O$ IN cm^{-1} AND VIBRATIONAL ASSIGNMENT[*1],[*2]

$Al(CH_3)_3\cdot(CH_3)_2O$ IR	$Al(CH_3)_3\cdot(CH_3)_2O$ Raman	$Al(CH_3)_3\cdot(CD_3)_2O$ Raman	Assignment
3028 w	3035 w D		CH_3 degenerate str. (OCH_3)
2983 m	2989 vw		
2953 sh	2957 m P		Overtone of CH_3 deform. (OCH_3)
2925 s	2926 m D	2925 m D	CH_3 degenerate str. ($AlCH_3$)
2889 m	2887 s P	2887 s P	CH_3 symmetric str. ($AlCH_3$)
2847 w	2842 m P		CH_3 symmetric str. (OCH_3)
2820 vw	2820 m P	2820 m P	Overtone of CH_3 deform. ($AlCH_3$)
	2787 vw P	2790 vw P	
		2282 w D	
		2250 m D	CH_3 degenerate str.
		2175 w P	
		2131 w P	Overtone of CD_3 deform.
		2081 s P	CD_3 symmetric str.
		2025 vw	
1462 s	1460 m D	1436 m D	CH_3 degenerate deform. ($AlCH_3$), CH_3 degenerate deform., CH_3 symmetric deform. (OCH_3)
1250 w			
1185 vs	1190 m P	1189 m P	CH_3 symmetric deform. ($AlCH_3$), CH_3 rock (OCH_3)
1153 m			
		1123 w P	CD_3 symmetric deform.
1046 vs	1052 w D	1062 m D	CO antisymmetric str. A″
891 s	894 m P	861 w	CO symmetric str. A′
710 s	716 m D	714 m D	AlC_3 degenerate str. A″, CH_3 rock ($AlCH_3$)
		684 w D	
622 m	625 m D	627 m D	AlC_3 degenerate str. A′
	576 w D	594 m P	
525 m	525 vs P	527 vs P	AlC_3 symmetric str. A′
473 m	470 w	456 m P	AlO str. A′
		414 vw	OC_2 scissors A′
		312 m D	
	233 w D	224 w D	AlC_3 symmetric deform. A′
	154 s D	152 s D	AlC_3 degenerate deform. A″

[*1] m, medium; s, strong; w, weak; v, very.

[*2] P, polarized; D, depolarized.

TABLE V. OBSERVED FREQUENCIES OF $[Al(CH_3)_2OCH_3]_3$ AND $[Al(CH_3)_2OCD_3]_3$ IN cm^{-1} AND VIBRATIONAL ASSIGNMENT

$[Al(CH_3)_2OCH_3]_3$		$[Al(CH_3)_2OCD_3]_3$	Assignment
IR	Raman	Raman	
	3064 vw		CH_3 degenerate str. (OCH_3)
2988 sh			
2954 sh	—2953 m P		Overtone of CH_3 deform. (OCH_3)
2934 s	—2935 m D	2935 m D	CH_3 degenerate str. ($AlCH_3$)
2895 w	—2894 s P	2895 s P	CH_3 symmetric str. ($AlCH_3$)
2853 m	—2854 m P		CH_3 symmetric str. (OCH_3)
2829 vw	—2828 w P	2831 m P	Overtone of CH_3 deform. ($AlCH_3$)
	2785 vw P	2785 vw P	
		2250 vw D	CD_3 degenerate str.
		2227 m P	
		2139 m P	Overtone of CD_3 deform.
		2086 s P	CD_3 symmetric str.
		2039 vw	
1457 m	—1458 w D	1434 w D	CH_3 degenerate deform. ($AlCH_3$), CH_3 degenerate deform., CH_3 symmetric deform. (OCH_3)
		1407 vw	
1256 vw			
1200 vs	—1201 m P	1207 m P	CH_3 symmetric deform. ($AlCH_3$), CH_3 rock (OCH_3)
		1140 vw	CD_3 degenerate deform.
		1069 w D	
1019 vw	—1018 m P	1000 m P	CO symmetric str. A_1'
987 vs	— 994 w D	981 w D	
		904 w	
686 vs	— 687 m D	685 m D	AlC_2 symmetric str. E', CH_3 rock ($AlCH_3$)
642 s			AlC_2 antisymmetric str. A_2''
	596 s P	598 s P	AlC_2 symmetric str. A_1'
567 vw	— 569 vw D	566 vw	Ring degenerate str. E'
437 m	— 440 vw	435 vw	
	380 s P	372 s P	Ring symmetric str. A_1'
305 m	— 309 vw	303 vw	Ring degenerate deform. E'
	251 vw	244 vw	
	207 vw	203 vw	
	141 m D	140 m D	AlC_2 degenerate deform. E'

were taken by the use of parallel and perpendicular Polaroid cylinders placed alternately over the Raman tube.

Results and Discussion

$Al(CH_3)_3 \cdot (CH_3)_2O$.—In Table I the expected types of skeletal vibrational modes and the number of skeletal vibrations in each species are shown. All of the 15 possible skeletal vibrations are both infrared- and Raman-active. The tentative assignments in the skeletal vibration region (720—130 cm^{-1}) are given in Table IV. The infrared and Raman intensities and polarization data of the Raman lines support these assignments. The assignments in the 720—350 cm^{-1} region agree precisely with those assignments which have been made by comparing the infrared spectra of several related substances.²⁾

Onishi showed that, for $Al_2(CH_3)_6$ and $Al_2(CH_3)_4Cl_2$, CH_3 symmetric deformation bands appear near 1200 cm^{-1} and that CH_3 rocking bands appear near 700 cm^{-1};³⁾ in accordance with these assignments, the bands near 1185 cm^{-1} and 710 cm^{-1} of $Al(CH_3)_3 \cdot (CH_3)_2O$ may be assigned to the CH_3 symmetric deformation ($AlCH_3$), superposed by CH_3 rocking (OCH_3), and to the AlC_3 degenerate stretching (A''), superposed by CH_3 rocking ($AlCH_3$), respectively.

As is shown in Table IV, $Al(CH_3)_3 \cdot (CH_3)_2O$ has seven to eight infrared bands and Raman lines in the 3100—2700 cm^{-1} region. These are very likely to be CH_3 degenerate stretchings, CH_3 symmetric stretchings, and overtones of CH_3 deformations of the $Al(CH_3)_3$ part and the $(CH_3)_2O$ part. The six Raman lines of $Al(CH_3)_3 \cdot (CD_3)_2O$ in the 2300—2000 cm^{-1} region are mainly due to

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3) T. Onishi, Dissertation, The University of Tokyo (1964).

TABLE VI. OBSERVED FREQUENCIES OF $[Al(C_2H_5)_2OCH_3]_3$ IN cm^{-1} AND VIBRATIONAL ASSIGNMENT

IR	Raman	Assignment
2989 sh		CH_3 degenerate str. (OCH_3)
2941 s	2937 m P	CH_3 degenerate str. (AlC_2H_5), Overtone of CH_3 deform. (AlC_2H_5, OCH_3)
2901 s	2897 w D	CH_2 antisymmetric str. (AlC_2H_5)
2865 s	2865 s P	CH_3 symmetric str. (AlC_2H_5, OCH_3)
2796 m	2792 m P	CH_2 symmetric str. (AlC_2H_5)
2731 w	2730 vw P	
1467 m 1454 m	1464 s D	CH_3 degenerate deform., CH_3 symmetric deform. (AlC_2H_5, OCH_3)
1411 m	1414 m D	CH_2 scissors (AlC_2H_5)
1376 w	1381 vw	
1254 w		
1223 w		
1197 s	1195 s P 1134 vw	CH_2 wag, CH_2 twist (AlC_2H_5), CH_3 rock (AlC_2H_5, OCH_3)
	1099 w	
1019 vw	1016 vw	CO symmetric str. A_1'
984 vs	988 s D	CC str.
956 w	962 vw	
918 m		
885 w		
848 w		
655 vs	650 m D	AlC_2 symmetric str. E′, CH_2 rock (AlC_2H_5)
632 m		AlC_2 antisymmetric str. A_2''
	568 s P	AlC_2 symmetric str. A_1'
540 vw 460 m	536 vw 449 w	Ring degenerate str. E′
	393 s P	Ring symmetric str. A_1'
351 m	339 vw	Ring degenerate deform. E′

CD stretchings of the $(CD_3)_2O$ part (Fig. 1a). The infrared and Raman spectra of $(CD_3)_2O$ and their assignments have been reported by Kanazawa and Nukada.[4] They assigned the Raman lines at 2230, 2202, and 2185 cm^{-1} to CD asymmetric stretchings; a strongly polarized line of a medium intensity at 2137 cm^{-1} to an overtone or to a combination of CD_3 deformation vibrations, and a strongly polarized line of a very strong intensity at 2053 cm^{-1}, to CD_3 symmetric stretching. By taking their assignments into consideration, four principal Raman lines of $Al(CH_3)_3\cdot(CD_3)_2O$ in the 2300—2000 cm^{-1} region may be assigned as is shown in Table IV. This assignment explains the intensity and polarization data satisfactorily. The 2175 cm^{-1} line (CH_3 degenerate stretching) is polarized; this may be due to the possible superposition of one of the overtones of the CD_3 deformations. Four lines, those at 3035, 2989, 2957, and 2842 cm^{-1}, of the eight Raman lines of $Al(CH_3)_3\cdot(CH_3)_2O$ in the 3100—2700 cm^{-1} region disappear in the spectrum of $Al(CH_3)_3\cdot(CD_3)_2O$. These four lines are evidently due to CH stretchings of the $(CH_3)_2O$ part. The remaining four lines, those at 2926, 2887, 2820, and 2787 cm^{-1}, which exist also in $Al(CH_3)_3\cdot(CD_3)_2O$, are due to CH stretchings of the $Al(CH_3)_3$ part. The 2926, 2887, and 2820 cm^{-1} lines are assigned to CH_3 degenerate stretching, CH_3 symmetric stretching, and an overtone of CH_3 deformation of the $Al(CH_3)_3$ part respectively. These considerations lead to the assignments in the 3100—2700 cm^{-1} region given in Table IV.

$[Al(CH_3)_2OCH_3]_3$.—Table II shows the expected types of skeletal vibrational modes and the number of skeletal vibrations in each species. The assignments in the skeletal vibration region (720—130 cm^{-1}) may be made tentatively as in Table V. The selection rule, the infrared and Raman intensities and the Raman polarization data support these assignments. The same consideration as in the case of $Al(CH_3)_3\cdot(CH_3)_2O$ leads to the identification of the bands near 1200 cm^{-1} and 686 cm^{-1} of $[Al(CH_3)_2OCH_3]_3$ as a CH_3 symmetric deformation ($AlCH_3$), superposed by CH_3 rocking (OCH_3) and an AlC_2 symmetric stretching (E′), superposed by CH_3 rocking ($AlCH_3$), respectively.

The infrared and Raman spectra of $[Al(CH_3)_2OCH_3]_3$ and $[Al(CH_3)_2OCD_3]_3$ in the 3100—2700 cm^{-1} region are quite similar to the spectra of $Al(CH_3)_3\cdot(CH_3)_2O$ and $Al(CH_3)_3\cdot(CD_3)_2O$ discussed above (Fig. 1b). Analogous considerations lead to the assignments in the 3100—2700 cm^{-1}

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[4] Y. Kanazawa and K. Nukada, This Bulletin, **35**, 612 (1962).

TABLE VII. OBSERVED FREQUENCIES OF $[Al(C_2H_5)_2OC_2H_5]_2$ AND $[Al(C_2H_5)_2OC_2D_5]_2$ IN cm^{-1} AND VIBRATIONAL ASSIGNMENT

$[Al(C_2H_5)_2OC_2H_5]_2$		$[Al(C_2H_5)_2OC_2D_5]_2$	Assignment
IR	Raman	Raman	
2977 m	—2974 w D		CH_3 degenerate str. (OC_2H_5)
2939 s	—2930 m P	2936 m P	CH_3 degenerate str. (AlC_2H_5), Overtone of CH_3 deform. (AlC_2H_5, OC_2H_5)
2901 s	—2898 w D	2901 w D	CH_2 antisymmetric str. (AlC_2H_5, OC_2H_5)
2864 s	—2865 s P	2867 s P	CH_3 symmetric str. (AlC_2H_5, OC_2H_5)
2791 w	—2791 w P	2790 m P	CH_2 symmetric str. (AlC_2H_5, OC_2H_5)
2727 w	—2729 w P	2730 w P	
		2231 s D	CD_3 degenerate str.
		2152 s P	Overtone of CD_3 deform.
		2113 sh	CD_2 antisymmetric str.
		2103 m P	CD_3 symmetric str.
		2073 m P	CD_2 symmetric str.
		2036 vw	
1482 w	—1458 s D	1468 m D	CH_3 degenerate deform., CH_3 symmetric deform. (AlC_2H_5, OC_2H_5), CH_2 scissors (OC_2H_5)
1462 sh			
1451 s			
1409 s	—1410 m D	1410 m D	CH_2 scissors (AlC_2H_5)
1394 s			
1288 m	—1295 w D		CH_2 wag, CH_2 twist (OC_2H_5)
1254 w			
1222 w			
1193 s	—1193 s P	1193 s P	CH_2 wag, CH_2 twist (AlC_2H_5), CH_3 rock (AlC_2H_5, OC_2H_5)
1100 s	—1118 w P	1123 w	
1058 vs	—1084 w D	1050 w D	CO asymmetric str. B_{2u}
985 s	— 990 m P	993 m P	CC str.
948 m	— 955 w P	953 w P	
914 w	— 928 w P	918 w P	
894 s			
806 s			
652 s			AlC_2 antisymmetric str. B_{1u}, CH_2 rock (AlC_2H_5)
	634 m D	644 m D	AlC_2 antisymmetric str. B_{2g}
		580 m D	
481 w			AlC_2 symmetric str. B_{3u}
	462 m P	439 s P	AlC_2 symmetric str. A_g
	380 m P	372 w P	Ring symmetric str. A_g

region described in Table V.

$[Al(C_2H_5)_2OCH_3]_3$.—In Table II the expected types of skeletal vibrational modes and the number of skeletal vibrations in each species are shown. The tentative assignments in the skeletal vibration region (720—130 cm^{-1}) are shown in Table VI. The selection rule, the infrared and Raman intensities and the Raman polarization data support these assignments. Although no deuterated compound such as $[Al(C_2H_5)_2OCD_3]_3$ has been studied, the assignment in the 3100—2700 cm^{-1} region may be made with certainty by taking the assignments of $[Al(CH_3)_2OCH_3]_3$ and $[Al(C_2H_5)_2OC_2H_5]_2$ (discussed below) into consideration (Table VI).

$[Al(C_2H_5)_2OC_2H_5]_2$.—In Table III the expected types of skeletal vibrational modes and the number of skeletal vibrations in each species are shown. The tentative assignments in the skeletal vibration region (720—130 cm^{-1}) shown in Table VII may be made. In assigning 652, 634, 481, and 462 cm^{-1} vibrations to AlC_2 stretchings B_{1u}, B_{2g}, B_{3u}, and A_g respectively, the assignments made by Onishi and Shimanouchi for $Al_2(C_2H_5)_6$ are taken into consideration (AlC_2 stretchings of $Al_2(C_2H_5)_6$: A_g 564 cm^{-1}, B_{1u} 662 cm^{-1}, B_{2g} 643 cm^{-1}, B_{3u} 546 cm^{-1}).[5] The selection rule, the infrared and Raman intensities and the Raman polarization data support these assignments. Hoffmann showed that, for $Al_2(C_2H_5)_6$, CH_2 rocking bands appear near 626 cm^{-1};[6] in accordance with this assignment, the infrared band at 652 cm^{-1} is assigned to AlC_2 antisymmetric stretching superposed by CH_2 rocking (AlC_2H_5).

As is shown in Table VII, $[Al(C_2H_5)_2OC_2H_5]_2$

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[5] T. Onishi and T. Shimanouchi, *Spectrochim. Acta*, **20**, 325 (1964).

[6] E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).

has six infrared bands and Raman lines in the 3100—2700 cm^{-1} region. These are very likely to be CH_3 degenerate stretchings, CH_2 antisymmetric strechings, CH_3 symmetric stretchings, CH_2 symmetric stretchings, and overtones of CH_3 deformations of the $Al(C_2H_5)_2$ part and the OC_2H_5 part. The six Raman lines of $[Al(C_2H_5)_2OC_2D_5]_2$ in the 2300—2000 cm^{-1} region are mainly due to CD stretchings of the OC_2D_5 group (Fig. 1c). These lines may be tentatively assigned as in Table VII. This assignment explains satisfactorily the intensity and polarization data. Only one Raman line at 2974 cm^{-1} among six Raman lines of $[Al(C_2H_5)_2$-$OC_2H_5]_2$ in the 3100—2700 cm^{-1} region disappears in the spectrum of $[Al(C_2H_5)_2OC_2D_5]_2$. Four Raman lines, those at 2936, 2901, 2867, and 2790 cm^{-1}, of $[Al(C_2H_5)_2OC_2D_5]_2$ are assigned to CH_3 degenerate stretching superposed by an overtone of CH_3 deformation, CH_2 antisymmetric stretching, CH_3 symmetric stretching, and CH_2 symmetric stretching of the C_2H_5 group attached to aluminum respectively. This assignment explains satisfactorily the infrared and Raman intensities and polarization data. These consideration lead to the assignments in the 3100—2700 cm^{-1} region given in Table VII.

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