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THE INFRARED SPECTRA OF PROPIONALDEHYDE AND PROPIONALDEHYDE-d_1*

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January 18, 1962

ABSTRACT

The infrared spectra of C_2H_5CHO and C_2H_5CDO from 4000 to 450 cm^{-1} have been observed and a tentative assignment of the observed bands has been made.

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INTRODUCTION

A sample of C_2H_5CDO was prepared and the vapor phase infrared spectra of C_2H_5CHO and the C_2H_5CDO were observed to determine the specificity of the deuteration. The vapor phase spectra of these compounds were not found in a search of the literature. Only the liquid phase Raman [1] and infrared [2,3] spectra of C_2H_5CHO have been reported.

The present investigation covers the infrared region from 450 to 4000 cm^{-1}. A tentative assignment of the observed bands has been made on the basis of isotope shifts and assignments in similar molecules.

EXPERIMENTAL AND RESULTS

Technical grade propionaldehyde was fractionally distilled in nitrogen atmosphere and the center fraction was transferred to a vacuum line where it was dried over anhydrous copper sulfate and further purified by trap-to-trap distillations in vacuum.

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[1] K. W. F. Kohlrausch and F. Koppl, Z. physik chem. B24, 370 (1934).

[2] American Petroleum Institute Project 44, Carnegie Institute of Technology. S. N. 1223.

[3] S. Pinchas, Anal. Chem. 27, 2 (1955).

The propionaldehyde-d_1 was synthesized using the reactions

$$RCOOR' \xrightarrow[AcOD]{Na} RCD_2OD + R'OD \qquad (1)$$

$$RCD_2OD \xrightarrow[K_2Cr_2O_7]{H_2SO_4} RCDO, \qquad (2)$$

where R is C_2H_5 and R' is C_5H_{11}. The deutero acetic acid was prepared from 99.5 per cent D_2O and freshly distilled acetic anhydride.

The procedure for reaction (1) given by Hill et al [4] was followed. The propanol-d_3 from Reaction (1) was separated from the reaction products by distillation and converted to the aldehyde by Reaction (2) using the procedure given by Blatt [5]. The propionaldehyde-d_1 obtained from the reaction was purified by gas chromatography, transferred to a vacuum line, dried over anhydrous copper sulfate and stored at dry ice temperature.

A sample of normal propionaldehyde was prepared by the same procedures. The infrared spectrum of this sample was identical with that of the sample of purified commercial propionaldehyde.

The spectra were recorded with a Perkin-Elmer Model 21 Infrared Spectrometer provided with NaCl and CaF_2 optics and with a Perkin-Elmer Model 12C Spectrometer provided with KBr optics. The spectral range from 450 to 4000 cm^{-1} was covered with these two instruments. A 10 cm cell with KBr windows and an 11 cm cell with NaCl windows were employed. All spectra were of vapors at pressures between 10 and 235 mm Hg.

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[4] D. G. Hill, W. A. Judge, P. S. Shell, S. W. Kanter and C. R. Hauser, J. Am. Chem. Soc. 74, 5599 (1952).

[5] A. H. Blatt, Organic Synthesis Vol. II (Wiley, New York, N. Y., 1943) p. 541.

Reproductions of the spectra are shown in Figs. 1 and 2. The conditions of observation are given in the figure captions. The frequencies and assignment of all the observed bands are given in Table 1.

DISCUSSION

Propionaldehyde and propionaldehyde-d_1 have, at most, C_s symmetry since the only element of symmetry possible is a single plane. The molecules have 15 a' and 9 a'' modes of motion and all the modes are infrared-active and Raman-active. An assignment of the fundamental modes for the two molecules is given in Table 2. The Raman frequencies in the table are from Kohlrausch and Koppl [1].

The C_2H_5 hydrogen strech and hydrogen deformation motions were assigned with reference to the corresponding assignments by Nolin and Jones [6] for 3-pentanone. The CH_2 twist and rock motions were assigned in accordance with assignments in paraffins [7]. The assignment of the motions involving the CCHO (CCDO) group followed directly from the observed frequency shifts on deuteration and from the corresponding assignments in the acetaldehydes [8].

The CH in-plane bend is set at 1395 cm^{-1} although a band was not observed in the infrared spectrum. The Raman frequency 1392 cm^{-1} can be assigned as this motion since this frequency is not found in the Raman spectrum of propionyl chloride [9]. No band was observed which could be assigned as the a'' CD wag, but the band should be found in the region 720 to 660 cm^{-1}. The band is expected to be very weak since, by analogy with the findings in the acetaldehydes [8], the band should

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[6] B. Nolin and R. N. Jones, J. Am. Chem. Soc. 75, 5626 (1951).

[7] J. K. Brown, N. Sheppard and D. M. Simpson, Phil. Trans Roy Soc. (London) A247, 35 (1954).

[8] J. C. Evans and H. L. Bernstein, Can. J. Chem. 34, 1083 (1956).

[9] K. W. Fritz Kohlrausch, Ramanspecktren (J. W. Edwards, Ann Arbor, Mich., 1945), p. 282-5.

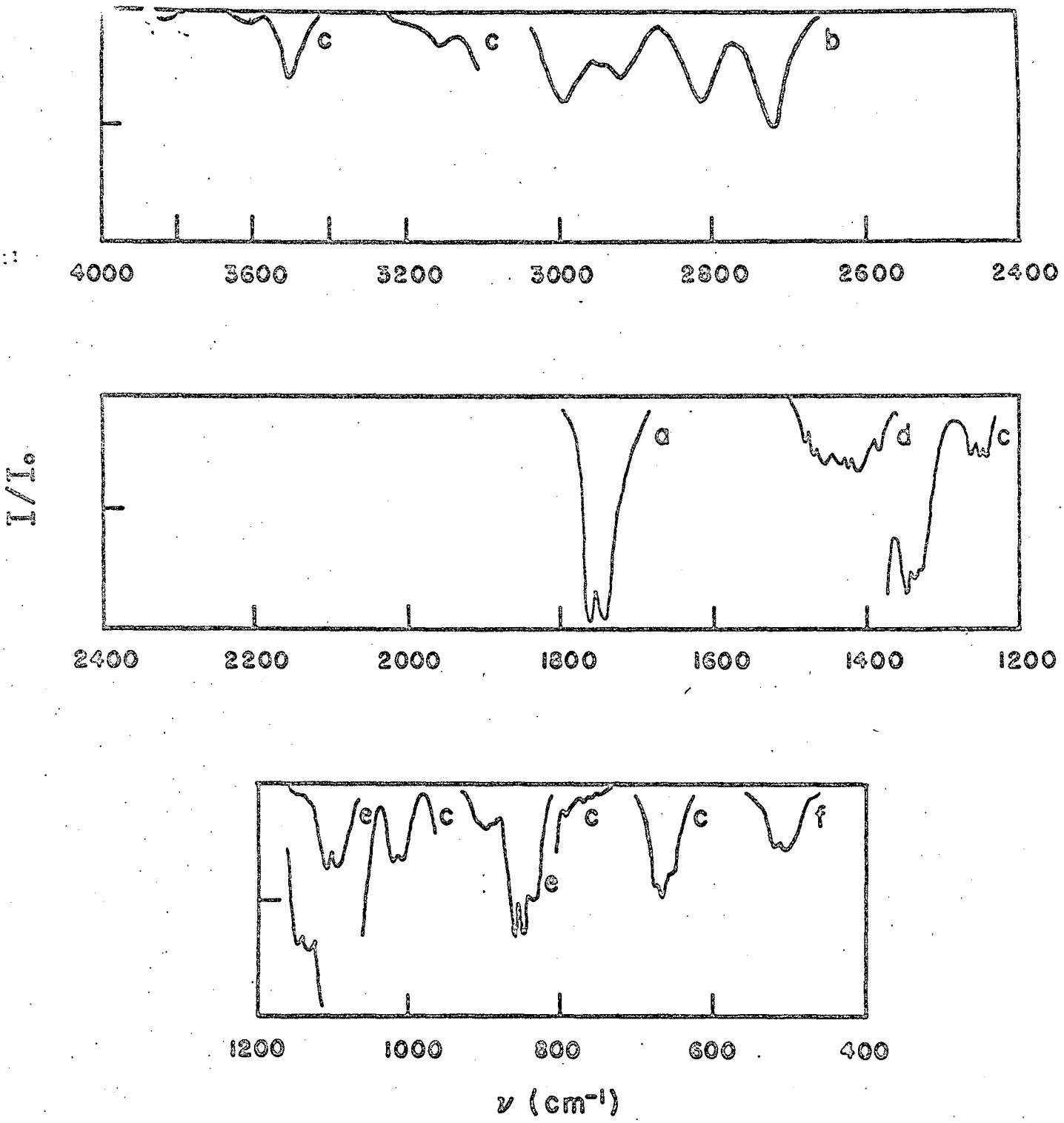

Figure 1. Spectrum of propionaldehyde, CH_3CH_2CHO. Optics (pressure in mm Hg): a, CaF_2 (10); b, CaF_2(20); c, NaCl (235); d, CaF_2 (40); e, NaCl (54); f, KBr (101).

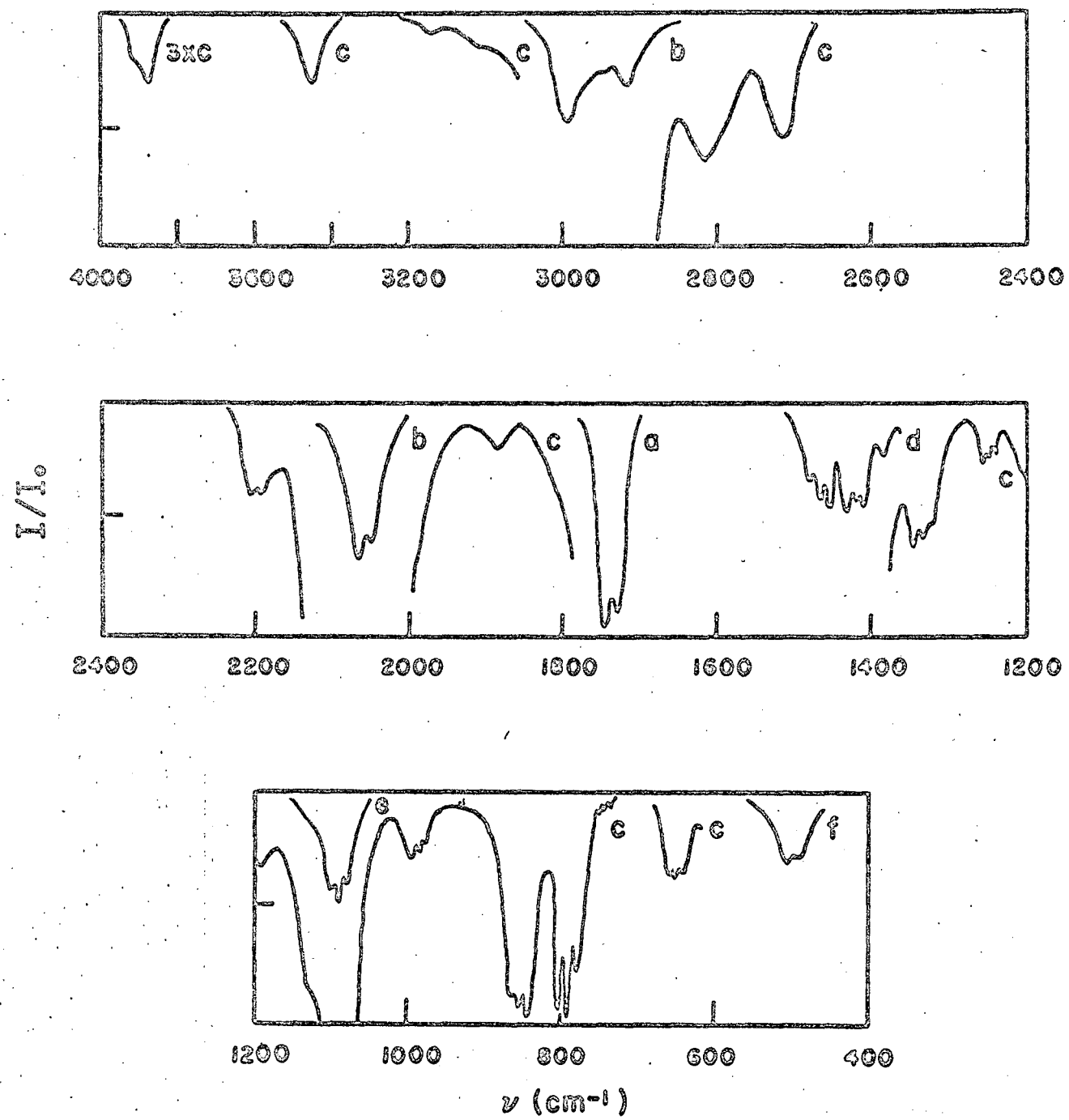

Figure 2. Spectrum of propionaldehyde-d_1, CH_3CH_2CDO. Optics (pressure in mm Hg): a, CaF_2 (10); b, CaF_2 (22); c, NaCl (235); d, CaF_2 (43); e, NaCl (34); f, KBr (101).

Table 1. Infrared frequencies (in cm^{-1}) of the propionaldehydes

CH_3CH_2CHO			CH_3CH_2CDO		
ν cm^{-1}	Intensity	Assignment	ν cm^{-1}	Intensity	Assignment
3840	w	2721 + 1105; 2993 + 850	3820	wsh	2993 + 856
			3780	w	2066 + 1730
3612	vw	2721 + 895			
3490	m	2 x 1750	3453	m	2 x 1730
3220	vw	2720 + 507			
3154	w	1750 + 1423	3170	vw	1730 + 1465
			3040	vwsh	2066 + 2 x 507
2993	vs	ν_2; ν_{16}	2993	vs	ν_2; ν_{16}
2943 (?)	vw	ν_{17}(?)	2946(?)	vw	ν_{17}(?)
2919	vs	$\nu_{1,3}$	2917	vs	$\nu_{1,3}$
2813	vs	Fermi doublet of 1400 overtones and ν_4	2815	w	1400 overtones
2721	vs	ν_4	2719	w	1350 overtones; Residual CH_3CH_2CHO
2504	vw	1423 + 1094	2539	vw	1465 + 1092
2402	w	1750 + 664	2427	vw	1334 + 1092
2331	vw	1468 + 848	2356	vw	1251 + 1099
			2316	vw	1465 + 856
2251	vw	1146 + 1105	2195	w	2 x 1092
2181	w	2 x 1094	2180	w	
2101	vw	1465 + 664			
2026	vw	1384 + 664	2066	vs	ν_4
1960	vw	1105 + 858	2050	vs	
1930	vw	1094 + 848			
1850	vw	1340 + 507	1887	w	1092 + 794; 1384 + 496
1763	vs	ν_5	1746	vs	ν_5
1744			1729		
1480			1478		
1468	s	ν_9	1465	s	ν_9
1456			1455		
1434			1430		
1423	s	ν_{10}	1419	s	ν_{10}
1410			1410		
1384	m	ν_8	1383	m	ν_8

Table 1. (continued)

CH_3CH_2CHO			CH_3CH_2CDO		
ν cm^{-1}	Intensity	Assignment	ν cm^{-1}	Intensity	Assignment
1349 1340 1332	m	ν_{12}	1344 1334 1324	m	ν_{12}
1261 1254 1247	w	ν_{19}	1257 1251 1241	w	ν_{19}
1146 1129	m	ν_6	1194 1134 1119? 1099	w wsh vwsh	ν_6(?) or combination ν_6
1105 1094	s	ν_7	1092 1080	s	ν_{13}; ν_7 Overlapped
1020 1003	m	2 x 507	995 984 978	m	2 x 496
907 895 883	s	ν_{11}	863 856 849	s	ν_{11}
858 848 836	s	ν_{20}	804 794 783	s	ν_{20}
791	vw	ν_{22}			
768 760 745	vw	ν_{21}	753 747 740	vw	ν_{21}
672 664 652	s	ν_{14}	660 653 644	s	ν_{14}
519 507	s	ν_{15}	509 496	s	ν_{15}

be weaker than the CH band in propionaldehyde which is a very weak band. The presence of a strong broad band at 653 cm^{-1} in propional-d_1 may make detection of the band difficult even with long path lengths. The Raman spectrum or the infrared spectrum of the solid may reveal the frequency of this mode.

The a' and a'' CH_3 rock motions were assigned to bands which behave in an analogous manner to bands observed in the corresponding acetaldehydes in this frequency region and assigned to these modes of motion. The frequency shifts observed upon deuteration are quite large for a group which is isolated from the site of deuteration, but the shifts undoubtedly result from interactions of the same nature as those proposed to explain the findings in the acetaldehydes [8].

Table 2. Assignments for the propionaldehydes[a]

Symmetry	Designation	Motion	CH_3CH_2CHO Infrared (cm^{-1})	CH_3CH_2CHO Raman (cm^{-1})	CH_3CH_2CDO Infrared (cm^{-1})
a'	ν_1	CH_3 sym. str.	2919	2939) Fermi 2883) doublet	2919
	ν_2	CH_3 asym. str.	2993	2978	2993
	ν_3	CH_2 sym. str.	2919	2939	2919
	ν_4	CH str.	2813) 2721)	2823) Fermi 2724) doublet	2050
	ν_5	CO str.	1744	1722	1729
	ν_6	CC str.	1129	1089	1134
	ν_7	CC str.	1094		1080
	ν_8	CH_3 sym. def.	1384		1383
	ν_9	CH_3 asym. def.	1468	1454	1465
	ν_{10}	CH_2 sym. def.	1423	1416	1419
	ν_{11}	CH_3 rock	895	893	856
	ν_{12}	CH_2 wag	1340	-	1334
	ν_{13}	CH wag	~1395	1392	1094
	ν_{14}	CCC def.	664	666	653
	ν_{15}	CCO def.	509	512	496
a"	ν_{16}	CH_3 asym. str.	2993	2978	2993
	ν_{17}	CH_2 asym. str.	2943	2939	2946
	ν_{18}	CH_3 asym. def.	1468	1454	1465
	ν_{19}	CH_2 twist	1254	1246	1251
	ν_{20}	CH_3 rock	848	846	794
	ν_{21}	CH_2 rock	760	-	747
	ν_{22}	CH wag	791	-	>660
	ν_{23}	CH_3 torsion	-	-	-
	ν_{24}	CHO torsion	-	-	-

[a] The Raman frequencies used in this assignment are from Kohlrausch. [9]

REFERENCES

[1] K. W. F. Kohlrausch and F.Koppl, Z. physik chem. B24, 370 (1934).

[2] American Petroleum Institute Project 44, Carnegie Institute of Technology. S. N. 1223.

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[5] A. H. Blatt, Organic Synthesis Vol. II (Wiley, New York, N.Y., 1943) p. 541.

[6] B. Nolin and R. N. Jones, J. Am. Chem. Soc. 75, 5626 (1951).

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[8] J. C. Evans and H. L Bernstein, Can. J. Chem. 34, 1083 (1956).

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