Raman Spectra of Hydrocarbons. V. nHexane, nHeptane, 2Methylpentane, 3 Methylpentane, 2,4Dimethylpentane, and 2,3Dimethylbutane

Forrest F. Cleveland and Pasquale Porcelli

Citation: The Journal of Chemical Physics **18**, 1459 (1950); doi: 10.1063/1.1747513
View online: http://dx.doi.org/10.1063/1.1747513
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/18/11?ver=pdfcov
Published by the AIP Publishing

Raman Spectra of Hydrocarbons. V. *n*-Hexane, *n*-Heptane, 2-Methylpentane, 3-Methylpentane, 2,4-Dimethylpentane, and 2,3-Dimethylbutane*

FORREST F. CLEVELAND AND PASQUALE PORCELLI†
Spectroscopy Laboratory, Department of Physics, Illinois Institute of Technology, Chicago 16, Illinois

(Received July 21, 1950)

Raman displacements, semiquantitative relative intensities, and quantitative depolarization factors are given for the above named hydrocarbons in the liquid state. The relative intensities and depolarization factors were obtained by use of a Gaertner microdensitometer. The depolarization factors were determined by a well-tested, single-exposure method. The previous data have been collected, tabulated, and compared with the present results, and probable values and average deviations are listed.

THE hydrocarbons used in this work were prepared under the direction of Professor C. E. Boord of the Department of Chemistry of the Ohio State University as part of the American Petroleum Institute Hydrocarbon Research Project in the Industrial Research Foundation of the University. The Raman spectral data were obtained by previously described[1] apparatus and methods.

n-HEXANE, $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

Raman displacements and estimated relative intensities for *n*-hexane have been obtained in 12 investigations,[2–13] but polarization data (largely qualitative) were obtained in only one of these.[12]

TABLE I. Raman spectral data for liquid *n*-hexane (C_6H_{14}).*

I PR	Δν PR	ρ PR	ρ HKW	N	Δν PV	AD
vw	148			1	148	
vw	169			1	169	
vw	189			1	189	
51	±309	0.78	*P*†	7	311	1.9
45	±335	0.37		6	333	1.8
83	±371	0.09	*P*†	9	368	2.6
56	±400	0.69		9	400	1.1
24	455	0.40		7	453	3.9
20	484			3	493	6.3
				3	729	0.7
				3	745	1.7
				1	760	
				1	794	
14	807	0.67	*P*	6	810	1.3
50	823	0.59		8	825	2.0
56	867	0.42	*P*	9	868	1.3
110	895	0.43	0.49	13	894	2.3
				4	899	1.0
10	949			7	951	2.1
12	975			7	973	3.6
18	1006	0.00	*P*	9	1007	1.6
54	1039	0.38	0.58	11	1039	1.3
49	1065			6	1064	1.2
69	1082	0.85	0.86	8	1080	1.5
54	1140	0.46	0.57	9	1138	2.2
19	1167	0.00		6	1166	1.0
vw	1196			4	1218	11.2
40	1287			4	1271	13.8
95	1304	0.78	0.80	9	1302	1.8
vw	1340			3	1340	2.0
vw	1366			3	1364	2.6
220	1440	0.85	0.86	7	1439	1.6
280	1459			7	1457	2.6
vw	1485			1	1485	
7	2667			4	2668	2.2
11	2700			2	2701	1.5
26	2730	0.30		8	2732	1.2
840	2850	0.27		8	2851	1.9
1000	2868		*P*	5	2863	1.2
				5	2876	1.0
				4	2899	2.5
750	2906	0.22	*P*	4	2914	4.0
720	2937	0.19		9	2938	1.6
450	2960	0.74		8	2963	1.4

* *I*=relative intensity; Δν=Raman displacement in cm^{-1}; ρ=depolarization factor; *PR*=present results; *HKW*=Herz, Kahovec, and Wagner (reference 12); *N*=number of times the line has been observed in apparently reliable independent investigations, including the present one; *PV*=probable value (mean of the *N* values); *AD*=average deviation of the *N* values from the mean; ± indicates lines that were observed both as Stoke's and anti-Stoke's lines; *P*=polarized; *vw*=very weak; and the braces join lines that were unresolved on the polarization spectrograms.

The present results, the previous polarization data, and the probable values of the Raman displacements are given in Table I. The probable values were obtained by taking a mean of all those values for a given line which seemed to be within the normal limits of experimental error. Some of the weak lines reported by only a few observers may result from impurities in the

TABLE II. Raman spectral data for liquid *n*-heptane (C_7H_{16}).*

I PR	Δν PR	ρ PR	ρ HKW	N	Δν PV	AD
				2	150	3.5
				2	203	4.5
				1	223	
				6	282	1.5
45	±281	0.23	*P*	11	310	1.2
130	±310			6	356	1.0
13	358			11	395	1.2
38	±395	0.83	*D*	1	405	
vw	454			7	451	3.0
				1	483	
vw	498			7	497	2.7
				2	505	0.5
				4	543	2.7
				1	696	
				4	722	2.7
vw	740			6	741	2.5
9	775	0.83		11	775	3.4
				1	805	
				1	826	
62	835	0.61	0.59	10	836	1.8
40	853	0.92		6	853	0.7
				1	868	
vw	881			6	886	2.0
69	902	0.40	*PP*	12	901	1.9
				2	907	0.0
vw	933			6	934	3.0
				1	949	
9	954	*D*		10	957	4.0
				1	988	
12	1027	0.87		7	1023	2.6
48	1047	0.69		8	1046	0.6
				2	1058	2.0
				1	1069	
68	1080	0.88	0.85	11	1081	2.2
52	1136	0.54	0.56	11	1136	1.6
18	1163	0.79		10	1161	1.0
				5	1206	1.7
				5	1243	4.2
				6	1265	3.3
				1	1281	
110	1305	0.87	0.89	12	1302	1.8
				1	1310	
				5	1345	2.2
				5	1365	2.4
320	1442	0.94	0.86	9	1438	2.4
	1459			9	1457	2.1
				1	1654	
				1	2523	
				1	2610	
				3	2666	5.7
				2	2708	1.5
				7	2732	0.8
24	2730	0.45		9	2852	2.7
870	2851	0.11	*P*	9	2873	2.0
1000	2870	0.10		6	2903	1.7
950	2903	0.16		2	2918	2.0
			P	11	2936	3.0
760	2932	0.07		10	2962	1.7
320	2958	0.87		1	2994	

* *D*=depolarized; *PP*=partly polarized; other symbols have the same meaning as in Table I.

* Presented in part at the Pittsburgh meeting of the American Physical Society, April 1944; abstract in Phys. Rev. **65**, 350 (1944).

† Present address: Department of Mathematics, University of Texas, Austin, Texas.

[1] F. F. Cleveland, J. Chem. Phys. **11**, 1, 227 (1943); **13**, 101 (1945).

[2] A. Petrikaln and J. Hochberg, Zeits. f. physik. Chemie **B3**, 217, 405 (1929).

[3] J. Okubo and H. Hamada, Science Reports Tôhoku Univ. **18**, 601 (1929).

[4] Godchot, Canals, and Cauquil, Comptes Rendus **194**, 176 (1932).

[5] Andant, Lambert, and Lecomte, Comptes Rendus **198**, 1316 (1934).

[6] K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).

[7] G. B. Bonino and R. Manzoni-Ansidei, Proc. Ind. Acad. Sci. **8A**, 405 (1938).

[8] Rosenbaum, Grosse, and Jacobson, J. Am. Chem. Soc. **61**, 689 (1939).

[9] H. Okazaki, J. Chem. Soc. Japan **60**, 559, 1269 (1939).

[10] Mizushima, Morino, and Takeda, Sci. Papers Inst. Phys. and Chem. Research (Tokyo) **38**, 437 (1941).

[11] Bazhulin, Plate, Sololova, and Kazanskii, Bull. Acad. Sci. URSS, sér. chim. (Russ) No. 1, 13 (1941).

[12] Herz, Kahovec, and Wagner, Monatshefte f. Chemie **76**, 100 (1946).

[13] N. Sheppard and G. J. Szasz, J. Chem. Phys. **17**, 86 (1949).

TABLE III. Raman spectral data for liquid 2-methylpentane (C_6H_{14}).

I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD	I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD
vw	182		1	182		3	1072		2	1071	1.0
14	328		3	323	3.0	1	1108		1	1108	
8	361		2	371	10.0	13	1149	0.91	3	1149	1.0
6	393		2	394	1.0	14	1175	0.73	2	1173	2.0
30	447	0.37	2	446	0.5	1	1240		2	1240	0.0
4	499		1	499		8	1301	0.90	2	1299	1.5
5	732		2	733	1.0	9	1340	0.93	2	1339	1.0
2	785		2	783	1.5	60	1443	0.91	2	1444	0.5
40	814	0.32	2	814	0.0	60	1463		2	1462	0.5
1	857		2	857	0.0	8	2722	0.93	1	2722	
9	890		3	890	0.0	30	2848		2	2847	0.5
4	936		1	936		1000	2875	0.42	2	2873	2.0
10	961	0.91	1	961		450	2910		2	2913	2.5
1	1016		1	1016		450	2934		2	2934	0.0
12	1039	0.92	2	1038	1.0	500	2963	0.69	2	2962	0.5

TABLE IV. Raman spectral data for liquid 3-methylpentane (C_6H_{14}).

I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD	I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD
21	393		2	390	3.0	36	1155		3	1157	1.0
43	443		2	444	1.0	23	1176		2	1175	1.0
			1	470		15	1281		2	1279	1.5
22	615		1	615		8	1316		2	1319	3.0
			1	736		18	1350	0.92	2	1352	2.0
50	745	0.58	3	747	1.0	2	1380		2	1379	0.5
			1	754		190	1446	0.93	2	1447	0.5
6	765		2	766	1.0	190	1460		2	1460	0.0
35	816	0.80	2	817	0.5	11	2735		1	2735	
22	876		3	877	1.7	650	2856		2	2856	0.0
24	954		3	957	6.3	900	2874	0.17	2	2876	2.0
25	977		2	983	5.0	700	2898		2	2899	0.5
34	1019		3	1017	2.0		2913		2	2913	0.0
		0.38	1	1038		1000	2934	0.21	2	2936	1.5
54	1042		1	1050		550	2961	0.56	2	2963	1.5

samples used. The 311 cm^{-1} line was resolved into the doublet 305, 317 in one investigation.[11] Measurement of depolarization factors in the 2900 cm^{-1} region was difficult because the lines were broad and overlapped each other.

n-HEPTANE, $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

Likewise, Raman displacements and estimated relative intensities for *n*-heptane have been obtained in 13 investigations,[6–18] but polarization data (again largely qualitative) were obtained in only one of these.[12]

The present results, the previous polarization data, and the probable values of the Raman displacements are given in Table II. Of the 16 lines observed in only a single investigation, 11 were reported by Okazaki[9] and 3 by Narayanaswamy.[18] Until verified with other carefully purified samples, these lines must be accepted with caution. The 1023 cm^{-1} line was resolved into the doublet 1021, 1031 by Okazaki.[9]

2-METHYLPENTANE, $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

Raman displacements and estimated relative intensities for 2-methylpentane have been obtained in only two investigations,[5,8] and no polarization data have been reported.[19]

The present results and the probable values of the Raman displacements are given in Table III. The doublet 936, 961 was reported as a single line in the previous work.[5,8] Because of overlapping lines, depolarization factors for some of the lines in the 2900 cm^{-1} region could not be obtained.

3-METHYLPENTANE, $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

Likewise, no polarization data have been reported for 3-methylpentane and Raman displacements and estimated relative intensities have been obtained in only two investigations.[5,8] The present results are given in Table IV.

TABLE V. Raman spectral data for liquid 2,4-dimethylpentane (C_7H_{16}).

I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD	I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD
			1	137		7	985		3	985	0.0
			1	149					1	996	
			1	169		5	1035		3	1035	1.3
12	183		2	181	2.0	3	1075		2	1076	1.0
40	308	0.59	3	308	0.3				1	1109	
4	329		2	333	3.5	60	1157	0.71	2	1157	0.0
			1	353		50	1169		2	1171	2.0
8	396		2	388	8.0	10	1232		2	1248	2.0
			1	419			1253				
14	446		1	446					1	1300	
50	470	0.06	3	469	0.3	33	1321	0.49	3	1320	1.0
			1	497		50	1348	0.66	3	1345	3.0
			1	687		100	1449	0.69	2	1449	0.0
			1	714		100	1461		2	1464	3.0
			1	728		23	2711		2	2714	3.0
200	808	0.00	3	807	0.3	70	2843		3	2842	1.0
10	866		3	869	1.7	1000	2872	0.07	3	2872	0.7
36	923	0.14	3	920	2.3	400	2883		1	2883	
			1	925		350	2914		3	2917	2.7
50	959	0.77	2	957	2.0	400	2934		3	2936	1.0
						800	2961	0.62	3	2964	2.7

TABLE VI. Raman spectral data for liquid 2,3-dimethylbutane (C_6H_{14}).

I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD	I PR	$\Delta\nu$ PR	ρ PR	N	$\Delta\nu$ PV	AD
			1	96		22	1161	0.79	3	1160	1.0
			1	220		13	1196	0.69	3	1197	1.0
7	271		1	271					1	1263	
9	289		3	291	1.0	15	1301		3	1300	0.7
11	346		3	346	0.0			0.91	1	1321	
			1	378		11	1345		3	1345	0.7
11	388		1	397		1	1381		2	1384	3.5
11	439		2	436	3.5	64	1447	0.80	2	1447	0.0
21	475		3	477	1.3	66	1468	0.80	2	1468	0.0
23	506		3	505	0.7				1	1478	
			1	629					1	2670	
100	728	0.01	3	728	0.0	4	2717		3	2718	1.0
30	753	0.08	3	755	1.0				1	2735	
2	819		2	817	2.0	3	2763		3	2760	2.3
			1	847					1	2774	
11	868	0.82	3	869	0.3	320	2857	0.06	3	2857	1.7
53	936	0.49	3	932	2.3	1000	2874	0.48	3	2873	1.3
50	946		4	943	2.2	760	2884		1	2884	
vw	955		3	955	0.3	560	2903		3	2903	0.0
11	1033	0.82	3	1033	0.3	830	2938		3	2936	1.0
2	1106		1	1106		850	2963		3	2963	1.3
5	1150		2	1150	0.0	400	2977		3	2980	1.7

[14] A. S. Ganesan and S. Venkateswaran, Ind. J. Phys. **4**, 195 (1929).
[15] G. B. Bonino and L. Brüll, Gazz. chim. Ital. **59**, 660 (1929).
[16] G. Collins, Phys. Rev. **40**, 829 (1932).
[17] S. C. Sirkar, Ind. J. Phys. **7**, 61, 257 (1932).
[18] P. K. Narayanaswamy, Proc. Ind. Acad. Sci. **26A**, 121 (1947).

[19] *Note added in proof:* In their literature search, the authors overlooked a paper by Fenske, Braun, Wiegand, Quiggle, McCormick, and Rank, Anal. Chem. **19**, 700 (1947), in which are given Raman displacements and approximate depolarization factors for some of the principal lines of each of the six compounds.

2,4-DIMETHYLPENTANE, $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

No polarization data have been reported for 2,4-dimethylpentane, but Raman displacements and estimated relative intensities have been reported twice.[7,8] The present results are given in Table V.

2,3-DIMETHYLBUTANE, $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

Raman displacements and estimated relative intensities have been reported three times[5,8,9] but no polarization data have been obtained. The present results are given in Table VI. The 1033 cm^{-1} line was resolved into the doublet 1029, 1039 by Okazaki.[9]

ACKNOWLEDGMENTS

The Hilger E-518 spectrograph used in this investigation was obtained in part with a grant from the Permanent Science Fund of the American Academy of Arts and Sciences. Most of the measurements for *n*-hexane and *n*-heptane were made by Mr. Donald E. Lee in 1944 and by Sisters Miriam Michael Stimson and Mary Agnita Reuter of Siena Heights College, Adrian, Michigan, during the summer of 1945. The authors are grateful for this assistance, and to Professor C. E. Boord and the American Petroleum Institute for furnishing the compounds.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 18, NUMBER 11 NOVEMBER, 1950

Asymmetry of Inner Electron Distributions in Homonuclear Diatomic Molecules

HOWARD REISS AND HOWARD SALTSBURG
Department of Chemistry, Boston University, Boston, Massachusetts

(Received July 17, 1950)

Disturbances in the distributions of inner shell electrons due to bond formation in homonuclear diatomic molecules have been investigated using a Fermi-Thomas type statistics. In the majority of molecules examined the disturbance seems to penetrate only to the shell directly beneath the valence shell.

Plots of the *number of electrons disturbed versus* atomic number are periodic, the disturbance being less for the alkali molecules than for the halogens. In any one group, these plots are remarkably linear. This behavior has permitted us to calculate the bond distance in Rb_2. It is found to be 4.28A. This value is to be compared with the distance 4.32A between nearest neighbors in the metal.

I. INTRODUCTION

THE role of inner shell electrons in chemical binding has always been a source of concern. James[1] has demonstrated that serious error can be introduced by ignoring their presence in Li_2. Van Vleck and Sherman[2] have appropriately referred to the phenomenon as the "Inner Shell Nightmare."

The participation of inner shells in bond formation should be observable in the distribution of electrons about the nucleus of a bound atom. Near the nucleus the distribution should be spherically symmetric; identical with that of an isolated atom. At points further removed from the nucleus (especially on the bond axis) elements of asymmetry should begin to appear. At one point this asymmetry will become so pronounced that by no stretch of the imagination will it be possible to regard the distribution as spherically symmetric. The fraction of electrons corresponding to the distribution beyond this point may be *defined* as *disturbed by the presence of the bond*, and may be used, as a measure of the depth of the disturbance caused by the binding process.

In this paper, an attempt will be made to establish a criterion by means of which the asymmetric point, mentioned above, can be located. This criterion will be used to estimate the number of electrons disturbed by the bonds in the homonuclear diatomic molecules of the halogen and alkali groups.

II. DESCRIPTION OF THE CRITERION

Electronic distributions will be determined through use of the Fermi-Thomas statistical method.[3-5] The problem of the isolated atom has been thoroughly

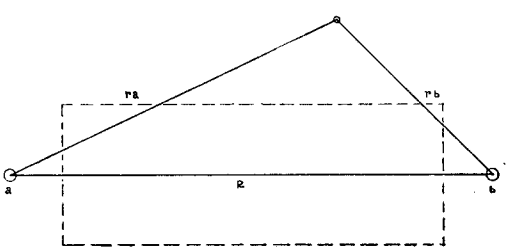

FIG. 1. Coordinate system.

[1] James, J. Chem. Phys. **2**, 794 (1934); Phys. Rev. **43**, 589 (1933).
[2] Van Vleck and Sherman, Rev. Mod. Phys. **7**, 168 (1935).
[3] Thomas, Proc. Camb. Phil. Soc. **23**, 542 (1927).
[4] Fermi, Zeits. f. Physik. **48**, 73 (1928).
[5] Fermi, Zeits. f. Physik. **49**, 550 (1928).